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On the Reflective Power of Some Eutectic Alloys in Relation to their Micro-Structures.

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I Introduction

To establish the relation between the reflective power of some alloys and their micro-structures is one of the most interesting and important problems, both from the theoretical point of view of the atomic or molecular construction of alloys and from the practical point of view of their colours. Despite the numerous investigations on the reflective power of several metallic elements and the alloys of definite compositions by Rubens and others, there is, as far as we know, none with respect to a system of alloys except those made by Professor Chikashige[1], in which he has succeeded in measuring the reflective power of several systems of alloys with respect to their micro-structures. We have, therefore, at the suggestion of Professor Chikashige, undertaken the present investigation, thereby confining the subject to the case of the binary eutectic alloys.

II Experimental method

According to Schwarzschild, there exist under a normal exposure the following relation with respect to the opacity:

$$D=AIT^{k} \quad \ldots\ldots(1)$$

or

$$\log D=A+\log I+K\log T \quad \ldots\ldots(2)$$

1 Zeit. f. Anorg. Chemie, **124**, 335 (1922); **194**, 334 (1926).

where D is the darkness produced by the light of the intensity I, exposed T seconds, and A and K are constants relating to the nature of the dry plate. The darkness in this relation is, we may add, equal to the logarithm of relative opacity, that is, the reciprocal value of relative transparencies measured by the transmitted rays of a monochromatic light through the unexposed and exposed position on the plate.

Keeping the time of exposure as a constant, if the opacities D and D' of the incident and reflected rays be known, we have the following relation for the reflective power R:—

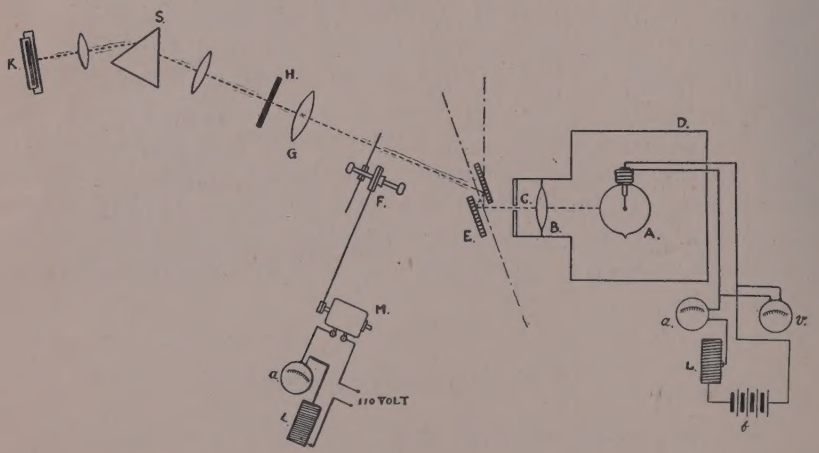
$$R=\frac{I}{I'}=\frac{D}{D'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Owing however to the difficulty of taking accurate measurements of them, we have not made use of the relative opacities but taken the times of exposure T and T' to produce the darkness D and D' with the light intensity I, so that we have

$$R=\frac{I}{I'}=\frac{D}{D'}=\left(\frac{T}{T'}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Our measurement relates therefore to the reflective power in terms of exposure with a knowledge of the characteristic constant K of a plate.

Fig. 1



The method of experiments runs as follows:—

The measuring arrangements, which have here in Professor Chikashige's laboratory hitherto been used, were slightly modified; it is as shown in Fig. 1, where A is a tungsten single filament lamp (8 volt ×

3 amperes), B a convex lens, which has its focus exactly at D, C a dark box, D a slit, E parallel mounted metallic sections, F a sector, G a concave lens forming an image of D at H, H the slit of the spectroscope, S a prism, and K a dry plate.

The light of a tungsten-lamp was, on the one hand, reflected twice by the polished surfaces of two samples placed parallel, the reflected light being dispersed by a prism and then photographed on a dry plate; while, on the other hand, the light coming directly from the light source, was dispersed by a prism and photographed on the same plate. The opacities of these two photograms were compared in the position of selected wave lengths corresponding with the seven visible colours measured in the Listing scale. The exact position of the spectra are to be known by reference to the annexed photos of the hydrogen and the mercury spectra.

In order to keep the light intensity constant for 3 to 4 hours, four accumulators were used, the current being adjusted to $\frac{1}{25}$ ampere. The incident ray kept an angle of 20° against the metallic section. The use of a collimating lens between D and E was thought unnecessary for the purpose of avoiding dispersion of the light from a slit D. The time of exposure was adjusted by a rotating sector F in which the aperture could be regulated to the exactness of 2°. The breadth of a slit H was kept as small as possible, so that the effect of the passing ray might be definite, as if a monochromatic light were used. The opacity was measured by means of Hartmann's micro-photometer in terms of its special scale. To express this scale in terms of the aperture, another standard "Wedge" was made, using a light source of constant intensity, with the aid of a sector belonging to the micro-photometer.

The darkness of the new scale was measured in terms of Hartmann's; the curve for calibration was drawn with photometric reading as abscissa and the angles of the sector as ordinate as shown in Fig. 4. By the use of this figure and of the relation (4), the reflective power may easily be calculated. As regards the measurement of the value of the constant K, the details will be given in Parag. 4, Section 4.

The Schwarzschild's formula necessitates our having the experiment carried on under a normal exposure. As log D and log T stand in a linear relation (2), the limit of exposure of the applied plate could however be known as described in Parag. 4, Section 1, by the use of an Ilford special rapid panchromatic plate exposed for several different times to a light having a constant intensity and developed, its darkness being then

determined by a thermopile. The result is represented in Fig. 3, from which the limit of the normal exposure of the plate is easily to be measured.

With a constant time of exposure, only a small range of the spectrum is liable to come into the limit of the normal exposure of the plate, and hence in order to have the reflective power measured for a wide range of the visible spectrum, it was necessary to take the photogram repeatedly with different appropriate times of exposure. This was however done, instead of changing the time, by changing the aperture of a sector at a constant time, as it was believed to be more advisable in avoiding personal errors in observation. The reflective power thus measured is the product of a two-fold reflection; the square root of the number must therefore be the real value sought.

III Preparation of the Sample, Polishing, Structure of the Polished surface, and Effect of Crystallizing Direction and Polarization

Melted alloys were furnace-cooled or sand-cast as the case might require. They were then annealed for 1–2 hours at a temperature 50°–100° lower than their solidifying points.

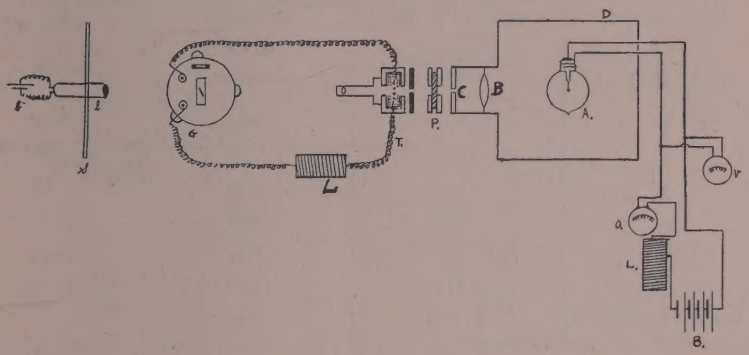
For the measurement of the reflective power of a sample, it is desirable that the polished surface should have an optical plane giving no scattering effect, but this is by no means a very convenient procedure by reason of its costing too much in labour and money. We, therefore, used an ordinary surface, except in a few cases, where we used an optical plane almost showing the linear flange of Newton's ring, whose number was less than six in the dimensions of the sample 20 mm × 15 mm. However, it was proved, at last, that neither result differs much from the other, as the experimental data afterwards given will show.

Whether the polished surface and the interior of a metal are different or not from each other in its structure, has hitherto often been a matter of discussion. Our experimental results incline rather to confirm, as may be seen from the numerical Tables given below, the opinion that both the surface and the interior are substantially the same.

Under the consideration that the crystallizing direction may have some influence upon the reflective power, several alloys consisting of fine crystals comparable to the breadth of the slit, from which the middle

parts only were used as sample, were prepared. Several points near the middle of the samples examined did not show any difference in their reflective powers, indicating that the crystallizing direction affects the

Fig. 2



reflection in no appreciable manner.

Lastly, the effect of the polarization has been neglected as not introducing any serious error in our experimental result.

IV Preliminary Experiments

(1) Determination of the Limit of Normal Exposure

If we could keep I constant in equation (2), it becomes a linear function,

$$\log D = A' + K \log T.$$

As this relation holds good only for a limited time of exposure, it is necessary, at first, to determine the range of time for the normal exposure. Availing ourselves of a sector, accessory to Hartmann's apparatus, we made for ourselves a photographic "Wedge," using a dry plate of the same kind as used throughout this investigation, and measured the light intensities transmitted through the exposed and unexposed positions on the "Wedge" by means of a thermopile of bismuth and antimony in terms of the deflection of Broker's galvanometer with the light source of a constant intensity.

The apparatus of measuring is shown in Fig. 2, where A is a light source, B a convex lens, C a slit in the dark box D, P a dry plate, T a thermopile, G a Broker's galvanometer, and L a rheostat.

The ratio of the two values of the exposed positions to the unex-

posed is a reciprocal of its relative transparency, *i.e.* relative opacity.

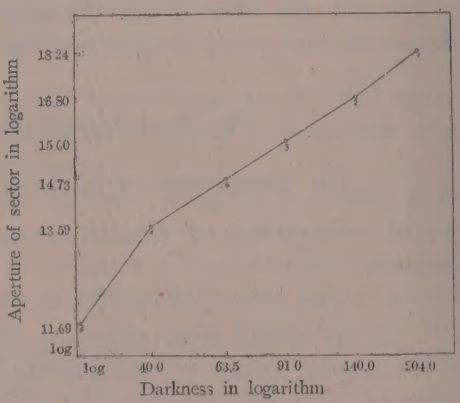
Experimental data are shown in Table I and represented graphically as in Fig. 3, from which it is evident, that the limit of normal exposure

Table I

Fixed position on a dry plate	Aperture of the sector at a corresponding position	Deflection of the galvanometer	Relative opacity
1	204·0	4·55	18·24
2	140·0	4·94	16·80
3	91·0	5·32	15·60
4	63·5	5·63	14·73
5	40·0	6·14	13·59
6	25·7	7·10	11·69
unexposed position	0	8·30	

falls between the photographic positions 2 and 5.

Fig. 3



The transmitted ray which passes through the "Wedge" includes the infra-red, but as its effect is inconsiderable, the relative opacity measured by the use of a thermopile can be held as tolerably accurate. The following experiment stands for this conclusion :—

The intensities of light cast directly upon a thermopile and that of the transmitted ray passing through the unexposed position on the "Wedge" were measured by means of a thermopile. These values are 12·2 and 3·6 in terms of the deflection of the galvanometer, showing that the infra-red is mostly absorbed by the glass plate and the gelatine film of the "Wedge."

(2) Calibration of the Scale of Hartmann's Photometer

As the scale of Hartmann's photometer is an equidistant one referred to a standard, its reading has no physical significance. In order to have this scale calibrated in terms of the time of exposure of a constant light

intensity, it was compared with the darkness of the same "Wedge" as was used in our determination of the normal exposure. So, we had the photometer's scale calibrated in terms of the aperture of the sector corresponding to the time of exposure in the limit of normal exposure.

The results of the experiments are as follows :—

Table II

Photometric reading	Aperture of the sector
29·0	40·0
36·0	60·0
48·0	94·0
53·0	109·0
62·0	141·0

These values are graphically represented as in Fig. 4 and from the graph are deduced the data given in Tab. III.

Fig. 4

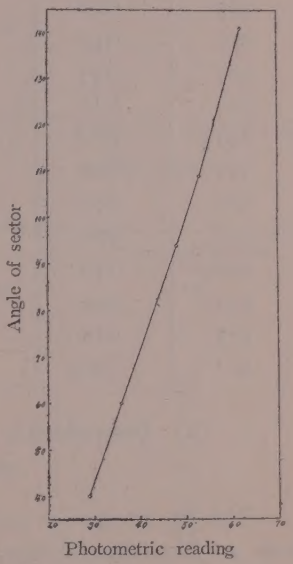


Table III

Photometric reading	Aperture of the sector	Photometric reading	Aperture of the sector	Photometric reading	Aperture of the sector
		49·5	98·18		
		49·0	96·83	36·0	60·00
63·0	145·2	48·5	95·28	35·5	58·88
62·5	144·2	48·0	94·00	35·0	58·01
62·0	141·0	47·5	92·69	34·5	56·82
61·5	138·7	47·0	91·41	34·0	55·59
61·0	136·8	46·5	89·74	33·5	54·52
60·5	134·9	46·0	88·11	33·0	53·33
60·0	132·9	45·5	86·30	32·5	51·88
59·5	131·2	45·0	84·72	32·0	50·58

59·0	128·8	44·5	83·17	31·5	49·49
58·5	127·3	44·0	81·85	31·0	47·75
58·0	125·6	43·5	80·26	30·5	46·08
57·5	123·9	43·0	78·88	30·0	44·32
57·0	122·5	42·5	77·09	29·5	42·36
56·5	121·0	42·0	75·68	29·0	40·00
56·0	118·6	41·5	74·30		
55·5	117·0	41·0	72·94		
55·0	115·0	40·5	71·61		
54·5	113·5	40·0	70·47		
54·0	112·2	39·5	69·18		
53·5	110·4	39·0	67·61		
53·0	109·0	38·5	66·37		
52·5	107·4	38·0	65·16		
52·0	106·2	37·5	63·66		
51·5	104·5	37·0	62·52		
51·0	102·6	36·5	61·37		
50·5	101·0				
50·0	99·54				

(3) Determination of the Wave-Length of a Spectrum developed on a plate

The line spectra of mercury and hydrogen were first photographed upon an Ilford special rapid panchromatic plate, using the same spectroscope as in the case of the measurement of reflective power. The characteristic lines were chosen and their positions were fixed in terms of the scale of Hartmann's photometer. The results are shown in Table IV.

Table IV

Spectrum	Wave length in Å	Position on the dry plate in mm
Hydrogen	6563	199·0
〃	4861	190·3
〃	4341	184·7
Mercury	5461	194·3
〃	4047	171·3

From the graph (Fig. 5) representing the relation between the

wave-lengths and the positions on the plate, we can easily determine the positions on the plate of the wave-lengths corresponding to the middle lines of the seven colours of the Listing scale. As to the red colour, however, the *C* line of the hydrogen spectrum was availed, the above graph not being used. The result is given in Table V.

Fig. 5

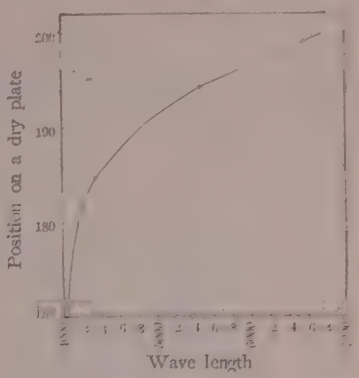


Table V

Wave length of the middle line of each of the seven colours in Listing scale in Å		Position on a dry plate in mm	Distance between two wave lengths in mm
Red	6563	190·0	0
Orange	6160	197·9	1·1
Yellow	5800	196·0	1·9
Green	5335	193·6	2·4
Blue	4735	189·2	4·4
Indigo	4395	185·3	3·9
Violet	4105	176·5	8·8

(4) Determination of the Characteristic Constant K of a dry Plate

From the Schwarzschild formula we have

$$\frac{D}{D'}=\frac{I}{I'} \quad \text{at a constant time of exposure,}$$

$$=\left(\frac{T}{T'}\right)^{k} \quad \text{at a constant intensity.}$$

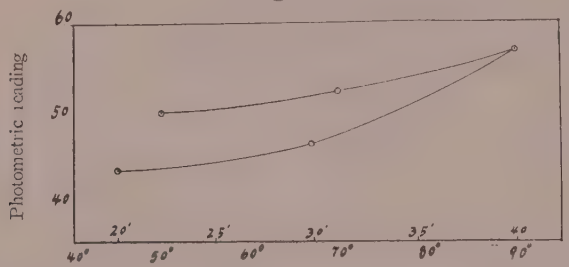
If we use a Nichol prism to regulate the light intensity, the tangent of the rotation angle of the prism is proportional to the light intensity, so that we have $\frac{I}{I'}=\frac{\tan a}{\tan a'}=\left(\frac{T}{T'}\right)^{k}$, where a and a' are the angles of rotation of the Nichol prism.

Then we have

$$K=\frac{\log\tan a-\log\tan a'}{\log T-\log T'} \quad \ldots\ldots\ldots\ldots\ldots (4)$$

Applying equation (4) in order to determine K, the two series of determinations about a relation between the darkness and the time of exposure at a constant intensity, and that between the darkness and the intensity at a constant time of exposure were made :—these results are given in Table VI and graphically represented in Fig. 6.

Fig. 6



Above line.....Angle of rotation of the Nichol ; under.....Time of exposure

Table VI

Photometric reading	Angle of rotation of the Nichol prism	Time of exposure in seconds
43·2	90·0°	20
49·2	90·0°	30
56·7	90·0°	40
52·1	70·0°	40
49·9	50·0°	40

From any two of the photometric readings, their corresponding times of exposure and the angles of rotation of the Nichol, we can calculate K according to relation (4). For example :—

Table VII

Photometric reading	Angle of rotation of the Nichol prism	Time of exposure in seconds
55·0	82·0°	37·8
50·0	53·5°	31·5

The value of K is 0·91.

(5) Effect of the Velocity of Rotation of a Metallic Sector upon the Value of the Darkness of a Plate

The number of rotations would theoretically have no effect upon

the intensity of the light, that is, the darkness of the plate. This fact is proved by taking photograms of the light with changing velocities of rotation of a metallic sector and by measuring their darkness on the plate. The number of rotations of a sector were 1150, 910 and 710 per minute. The resulting darkness of the plate measured by Hartmann's photometer was then almost equal to each other, the differences being within $\pm 0{\cdot}1$ in the photometer reading.

(6) Constancy of the Intensity of the Light Source

During three hours, which was the time required for one course of our experiments, several photograms of the light source were taken, the darknesses of which were measured by the photometer in the same manner as before; the deviation of photometric readings was then found always to be within $\pm 0{\cdot}1$. We may therefore safely conclude that there was no appreciable change of intensity during a single course of the experiment.

(7) Effect of the Application of a Collimating Lens in the Determination of the Reflective Power

For the measurement of the reflective power, whether the application of a collimating lens between a slit C and the sample E (Fig. 1) acts to prevent or not the diversion of the ray from the light source was not certain. So, the reflective power of pure silver was tested for a light of different wave lengths, 6563–4735 Å, with and without a collimating lens. The result indicated that there was no effect upon the values of the reflective power, as shown in the following Tables VIII and IX.

Table VIII

Without a collimating lens

Wave length	6563	6160	5800	5335	4735
Photometric reading with direct exposure	56·4	55·2	55·4	53·6	49·2
Aperture of the sector deduced from Fig. 4	120·53	115·80	116·60	110·76	97·37
Photometric reading with reflected ray of silver	53·5	48·9	47·6	45·2	41·5
Aperture of the sector deduced from Fig. 4	110·40	96·52	92·99	85·22	74·32
Reflective power after two-fold reflection	91·60	83·34	79·71	76·82	76·31
Reflective power	95·71%	91·30%	89·28%	87·70%	87·36%

Table IX

With a collimating lens

Wave-length	6563	6160	5800	5335	4735
Photometric reading with direct exposure	47·0	45·9	46·1	44·8	41·3
Aperture of the sector deduced from Fig. 4	91·41	87·75	88·43	84·10	73·75
Photometric reading with reflected ray of silver	44·7	41·1	40·0	37·9	34·3
Aperture of the sector deduced from Fig. 4.	83·76	73·21	70·47	64·77	56·32
Reflective power after two-fold reflection	91·67	83·43	79·68	77·02	76·37
Reflective power	95·75%	81·34%	89·27%	87·76%	87·40%

(8) Regulation of the Intensity of the Light Source

When a sample has a low reflective power, it is impossible to insure that the darkness in photograms of the incident and the reflected rays fall into the limit of the normal exposure with the same time of exposure, and therefore we must have recourse to changing the intensity of the light source by use of the "Wedge." Before use, this "Wedge" was naturally tested for the ability of having the same absorption of the light along the range of the visible spectrum, *i.e.* whether it has a neutral tint or not. Several photograms of the spectrum were therefore taken for this purpose, using different positions on the "Wedge" in a constant time of exposure. From these values of the darkness the aperture of the sector was measured. The ratio of these values at 6563 Å to any other wave-lengths was calculated. The following example may show how the absorbing power of a "Wedge" was determined.

Table X.

Fixed position on the "Wedge"		(7)
Photometric reading		61·0
Aperture of the sector deduced from Fig. 4	t	136·80
Fixed position on the "Wedge"		(4)
Photometric reading		45·9
Aperture of the sector deduced from Fig. 4	t'	87·91
Ratio of absorption power	$\left(\frac{t'}{t}\right)^K$	66·87

The ratio of absorption of the different positions on the applied "Wedge" is as follows:—

Table XI

Position on the "Wedge"	4/7	4/6	2/7	III/VII	II/VII	I/VII
Ratio of absorption	66·87	78·17	43.86			
"				14·75	12.18	8·43

As may be seen from the following Table, the ratios are almost the same, notwithstanding the change of positions on the "Wedge" or omitting the "Wedge." The applied "Wedge" has therefore a neutral tint.

Table XII

Wave length	6563	6160	8500	5335	4735
Fixed position on the "Wedge"	(2)	(2)	(2)	(2)	(2)
Photometric reading with direct exposure	53·8	52·4	52·6	50·9	46·6
Aperture of the sector deduced from Fig. 4	111.48	107·16	107·72	102·28	90.07
Ratio of the aperture of the sector to that of 6563 Å		96·19%	96·69%	91·40%	80·80%
Fixed position on the "Wedge"	(4)	(4)	(4)	(4)	(4)
Photometric reading with direct exposure	56·8	55·6	55·8	54·0	49·6
Aperture of the sector deduced from Fig. 4	121·90	117·32	117·96	112·20	98·49
Ratio of the aperture of the sector to that of 6563 Å		96·24%	96·77%	92·00%	80·80%
Fixed position on the "Wedge"	(6)	(6)	(6)	(6)	(6)
Photometric reading with direct exposure	58·7	57·1	57·5	55·6	51·6
Aperture of the sector deduced from Fig. 4	127·90	122·78	123·90	117·32	104·84
Ratio of the aperture of the sector to that of 6563 Å		96·00%	96·87%	91·73%	80·87%
Fixed position on the "Wedge"	(7)	(7)	(7)	(7)	(7)
Photometric reading with direct exposure	61·0	59.6	59·9	58·0	53 5
Aperture of the sector deduced from Fig. 4	136 80	131·56	132·56	124·60	110·40
Ratio of the aperture of the sector to that of 6563 Å		96·18%	96·92%	91·88%	80·72%
Photometric reading with direct exposure	56·4	55·2	55·4	53·6	49·2
Aperture of the sector deduced from Fig. 4	120·52	115·80	116·60	110·76	97·37
Ratio of the aperture of the sector to that of 6563 Å		96·1%	96·8%	91·9%	80·8%

The absorbing power of a "Wedge" cannot however be maintained constant for a long period, so that another set was necessary to be kept as a reserve.

(9) The Exactness of the Measurement of the Reflective Power.

The experimental error of the reading of Hartmann's photometer was always within $\pm 0{\cdot}1\%$, so that the calculated error of the reflective power must be within $\pm 0{\cdot}2\%$.

By comparing the values of our determination of the reflective power of pure silver and of copper to those obtained by interpolation of Hagen and Rubens's results, we see there exists no much deviation as the following Tables will show :—

Table XIII

Reflective Power of Silver

Wave length	6563	6160	5800	5335	4735	4395	4105
Hagen and Ruben	96·3%	91·2%	89·3%	87·9%	87·4%	85·4%	82·1%
The investigator	95·71%	91·30%	89·28%	87·70%	87·36%	85·88%	82·02%

Table XIV

Reflective Power of Copper

Wave length	6563	6160	5800	5335	4735	4395	4105
Hagen and Ruben	80·4%	74·6%	62·5%	46·7%	40·3%	35·6%	31·3%
The investigator	82·79%	75·65%	63·20%	43·30%	42·76%	40·31%	

(10) Influence of the Mode of Casting upon the Reflective Power of the Alloys

Five samples of the silver and copper eutectic were made in the following different ways :—

Sample a : Cast in an iron mould

〃 b : Cast in a sand mould at a temperature of 200°

〃 c : Cast in a sand mould at a temperature of 100°

〃 d : Annealed at 650° for 3 hours

〃 e : Quenched at 650°

These samples were polished and etched with a 5% ferric chloride solution. They showed no blow holes under a microscope of 520 times magnification. Their reflective powers determined are tabulated as follows :—

Table XV
Reflective Power

Wave length		6563	6160	5800	5335	4735	4395
Sample	a	72·94%	71·13%	69·57%	65·30%	62·50%	53·85%
"	b	81·65%	79·58%	77·76%	73·29%	69·98%	59·85%
"	c	80·80%	78·67%	76·79%	77·21%	69·31%	59·13%
"	d	81·80%	79·66%	77·86%	73·26%	70·05%	59·97%
"	e	72·18%	70·21%	68·73%	64·72%	61·77%	55·33%

Table XVI
Sample a

Wave length	6563	6160	5800	5335	4735	4395
Photometric reading with direct exposure	58·7	56·7	57·7	55·8	50·3	58·0
Aperture of the sector deduced from Fig. 4	127·30	121·30	124·24	117·96	100·41	125·60
Position on the "Wedge"	4	4	4	4	4	4
Photometric reading of the sample	56·2	51·8	51·7	45·65	38·8	36·2
Aperture of the sector deduced from Fig. 4	119·48	105·27	105·10	86·81	67·11	60·52
Position on the "Wedge"	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	53·20	50·59	48·40	42·64	39·06	29·00
Reflective power	72·94	71·13	69·57	65·30	62·50	53·85

Sample b

Wave length	6563	6160	5800	5335	4735	4395
Photometric reading with direct exposure	55·8	56·7	57·7	55·8	50·3	58·0
Aperture of the sector deduced from Fig. 4	118·03	121·30	124·24	117·96	100·41	125·60
Position on the "Wedge"	4	4	4	4	4	4
Photometric reading of the sample	62·15	60·45	59·5	53·9	45·4	42·3
Aperture of the sector deduced from Fig. 4	141·94	134·71	131·15	111·88	86·04	76·32
Position on the "Wedge"	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	66·66	63·33	60·86	53·71	48·97	35·82
Reflective power	81·65	79·58	77·76	73·29	69·98	59·85

Sample c

Wave length	6563	6160	5800	5335	4735	4395
Photometric reading with direct exposure	55·8	56·7	57·7	55·8	50·3	58·0
Aperture of the sector deduced from Fig. 4	118·03	121·30	124·24	117·96	100·41	125·60
Position on the "Wedge"	4	4	4	4	4	4
Photometric reading of the sample	61·5	59·55	59·4	52·8	41·6	41·5
Aperture of the sector deduced from Fig. 4	138·71	131·39	130·56	108·45	74·66	74·31
Position on the "Wedge"	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	65·28	61·89	58·96	52·21	43·04	34·96
Reflective power	80·80	78·67	76·79	72·26	69·31	59·13

Sample d

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	56·4	55·2	55·4	53·6	49·2	56·5	59·7
Aperture of the sector deduced from Fig. 4	120·52	115·80	116·60	110·76	97·37	121·00	131·88
Position on the "Wedge"							4
Photometric reading of the sample	49·2	46·0	44·9	39·9	34·4	31·4	30·4
Aperture of the sector deduced from Fig. 4	97·33	88·20	84·48	70·07	56·62	49·37	46·28
Position on the "Wedge"							7
Ratio of absorption							66·87
Reflective power after two-fold reflection	66·92	63·46	60·63	53·60	49·64	35·96	21·71
Reflective power	81·80	79·66	77·86	73·21	70·05	59·97	46·60

Sample e

Wave-length	6563	6160	5800	5335	4735	4395
Photometric reading with direct exposure	58·5	56·7	57·7	55·8	50·3	58·0
Aperture of the sector deduced from Fig. 4	127·30	121·30	124·24	117·96	100·41	125·60
Position on the "Wedge"	4	4	4	4	4	4
Photometric reading of the sample	55·4	50·9	50·9	45·1	37·5	35·7
Aperture of the sector deduced from Fig. 4	116·77	102·30	102·31	85·11	63·76	59·25
Position on the "Wedge"	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	52·10	49·29	47·24	41·88	38·15	28·45
Reflective power	72·18	70·21	68·73	64·72	61·77	53·33

The reflective powers of the samples d and b are equal and highest. Those of the other samples are lower and decrease in order from c, a to e, the order being kept precisely the same in all wave-lengths. From this fact that the effect of casting upon the reflective power is not specific, we may draw the following conclusion, that the lowering of the refleective power is certainly due to the scattering effect of some tiny blow holes which are not detectable under a microscope.

V The Results of the Experiments

(1) The System of Silver and Copper

This system has already been studied by Nosé[1]; our result comes only to verify his results in all respects. As for materials, silver with a fineness of 999·9 per mil and electrolytic copper of the finest quality were used. The metals, mixed in the required weight proportion, were melted in Tammann's porcelain tubes, and the melted alloys were cast each in a sand mould at a temperature of 200°, and annealed for 3 hours at 650°, while the pure silver and the copper were annealed at a temperature 100° and 150°, respectively, below their melting-points. During the process of the melting and annealing, the surface of the alloys was always covered with charcoal powder under a current of carbon dioxide to prevent oxidation. Each sample was then polished first on emery paper, and then on a pitch plate with the aid of rouge. They were carried to a very high degree of ordinary hand polishing but not precisely to an optical plane.

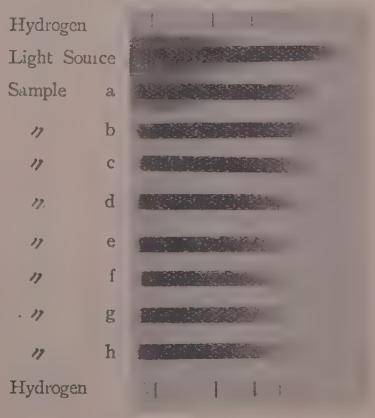
The samples examined had the following compositions:—

Table XVII
Composition of the Samples

No. of samples	a	b	c	d	e	f	g	h
Percentage of silver	0	2	15	28	50	80	90	100
Percentage of copper	100	98	85	72	50	20	10	0

The photograms of the spectra of the reflected rays, together with the spectrum of the light source, are given in Fig. 7. From the photographic plates was determined the percentage of reflective power in comparison with that of the direct light of an electric lamp regarded as 100. The results of examination are shown in Table XVIII for each sample and summarized in Table XIX.

Fig. 7.



1 Zeit. f. Anorg. Chemie, **154**, 344 (1926).

Table XVIII:—

Sample a

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	50·6	53·25	55·4	53·6	49·2	56·5	59·0
Aperture of the sector deduced from Fig. 4	101·52	109·76	116·60	110·76	97·37	121·00	128·80
Position on the "Wedge"	—	—	—	—	—	—	—
Photometric reading of the sample	59·2	61·45	54·7	51·4	46·8	52·9	51·5
Aperture of the sector deduced from Fig. 4	129·45	138·56	114·01	104·08	90·83	108·62	104·62
Position on the "Wedge"	—	—	—	—	—	—	—
Ratio of absorption	—	—	—	—	—	—	—
Reflective power after two-fold reflection	91·60	83·34	79·71	76·82	76·31	73·68	67·28
Reflective power	95·71	91·30	89·28	87·70	87·36	85·88	82·02

Sample b

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	50·6	55·2	55·4	53·6	49·2	56·5	59·0
Aperture of the sector deduced from Fig. 4.	101·52	115·80	116·60	110·76	97·37	121·00	128·80
Position on the "Wedge"	—	—	—	—	—	—	—
Photometric reading of the sample	58·75	46·0	51·55	49·65	44·5	49·15	48·15
Aperture of the sector deduced from Fig. 4.	127·99	106·22	104·76	98·58	83·08	97·20	94·34
Position on the "Wedge"	—	—	—	—	—	—	—
Ratio of absorption	—	—	—	—	—	—	—
Reflective power after two-fold reflection	82·36	75·15	73·75	73·11	70·36	66·60	61·24
Reflective power	90·75	86 70	85·88	85·50	83·88	81·61	78·26

Sample c

Weve-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	56·4	55·2	55·4	53·6	49·2	56·5	59·0
Aperture of the sector deduced from Fig. 4.	120·52	115·80	116·60	110·76	97·37	121·00	128·80
Position on the "Wedge"	—	—	—	—	—	—	—
Photometirc reading of the sample	49·2	46·0	46·0	39·9	34·4	45·6	44·55
Aperture of the sector deduced from Fig. 4.	97·33	88·20	84·48	70·07	56·62	86·75	83·35
Position on the "Wedge"	—	—	—	—	—	—	—
Ratio of absorption	—	—	—	—	—	—	—
Reflective power after two-fold reflection	66·92	63·46	60·63	53·60	49·64	60·05	54·71
Reflective powir	81·80	79·66	77·86	73·21	70·05	77·50	73·96

Sample d

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading withdirect exposure	56·4	55·2	55·4	53·6	49·2	56·5	59·7
Aperture of the sector deduced from Fig. 4.	120.52	115·80	116.60	110.76	97·37	121.00	131·88
Position on the "Wedge"							4
Photometric reading of the sample	49·2	46·0	44·9	39·9	34·4	31·4	30·4
Aperture of the sector deduced from Fig. 4.	97·33	88.20	84·48	70.07	56.62	49·37	46.28
Position on the "Wedge"							7
Ratio of absorption							66.87
Reflective power after two-fold reflection	66.92	63·46	60.63	53.60	49.64	35.96	21·71
Reflective power	81·80	79.66	77·86	73·21	70.05	59.97	46.60

Sample e

Weve-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	49·4	50·6	55·8	54·0	61·2	62·1	62·9
Aperture of the sector deduced from Fig. 4.	97·33	101·32	117·96	112.20	137·56	141·56	145·00
Position on the "Wedge"	4	4	4	4	4	3	3
Photometric reading of the sample	62·1	61·5	59·6	51·0	49·4	47·4	32·5
Aperture of the sector deduced from Fig. 4.	140.10	138.07	131·55	102.61	97.85	92.52	51.87
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	66.87	66.87	66.87	66.87	66.87	59.64	59.64
Reflective power after two-fold reflection	78·51	74·69	62.24	51.96	41·34	34.49	19.93
Reflective power	88.61	86.43	78.90	72.09	64.30	58.73	44.65

Sample f

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	49·4	55·6	55·8	54·0	61·2	62·1	62·9
Aperure of the sector deduced from Fig. 4.	97·33	117·32	117·96	112.20	137·56	141·56	145·00
Position on the "Wedge"	4	4	4	4	4	3	3
Photometric reading of the sample	57·5	59·4	46·8	32·4	34·6	32·4	29·6
Aperture of the sector deduced from Fig. 4.	123·29	130·15	90·59	51·81	57·09	51·56	42·57
Position on the "Wedge"	6	6	6	6	7	7	7
Ratio of absorption	78·17	78·17	78·17	78·17	66.87	59.64	59.64
Reflective power after two-fold reflection	89·55	71·38	51·09	32·16	25·32	20.26	16.65
Reflective power	89·75	84·49	71·48	56·71	50·32	45·01	40.81

Sample g

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	45·95	55·6	55·8	54·0	61·2	62·1	62·9
Aperture of the sector deduced from Fig. 4.	87·23	117·32	117·96	112·20	137·56	141·56	145·00
Position on the "Wedge"	4	4	4	4	4	2	2
Photometric reading of the sample	62·1	56·55	45·1	30·3	31·2	29·2	31·4
Aperture of the sector deduced from Fig. 4.	141·32	121·16	84·91	45·40	49·90	40·82	48·99
Position on the "Wedge"	6	6	6	6	7	7	7
Ratio of absorption	78·17	78·17	78·17	78·17	66·87	66·87	43·86
Reflective power after two-fold reflection	85·77	66·91	48·17	28·52	22·40	18·18	14·70
Reflective power	92·61	81·80	69·41	51·80	47·33	42·65	38·35

Sample h

Wave-length	6563	6160	5800	5335	4735	4395
Photometric reading with direct exposure	49·4	55·6	55·8	53·7	60·7	62·1
Aperture of the sector deduced from Fig. 4.	97·33	117·32	117·96	111·20	135·68	141·56
Position on the "Wedge"	4	4	4	3	3	3
Photometric reading of the sample	56·4	56·15	43·7	30·2	29·7	29·1
Aperture of the sector deduced from Fig. 4.	120·66	119·32	80·81	45·14	43·04	40·46
Position on the "Wedge"	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	59·64	59·64	59·64
Reflective power after two-fold reflection	68·53	57·23	39·95	22·36	18·28	16·25
Reflective power	82·79	75·65	63·26	47·30	42·76	40·31

Table XIX

The Reflective Power of the System of Silver and Copper

Wave length	6563	6160	5800	5335	4735	4395	4105
Sample a	95·71%	91·30%	89·28%	87·70%	87·36%	85·88%	82·02%
" b	90·75%	86·70%	85·88%	85·50%	83·88%	81·61%	78·26%
" c	90·12%	83·08%	82·81%	82·42%	78·67%	77·50%	73·96%
" d	81·89%	79·66%	77·86%	73·21%	70·05%	59·97%	46·60%
" e	88·61%	86·43%	78·90%	72·09%	64·30%	58·73%	44·65%
" f	89·75%	84·49%	71·48%	56·71%	50·32%	45·01%	40·81%
" g	92·61%	81·80%	69·41%	51·80%	47·33%	42·65%	38·35%
" h	82·79%	75·65%	63·20%	47·30%	42·76%	40·31%	

The reflective power in reference to a single wave-length and that in reference to the composition are graphically, represented in Figs. 8 and 9 respectively, and the dimentional relation between these 3 factors

Fig. 8.

System of Ag–Cu

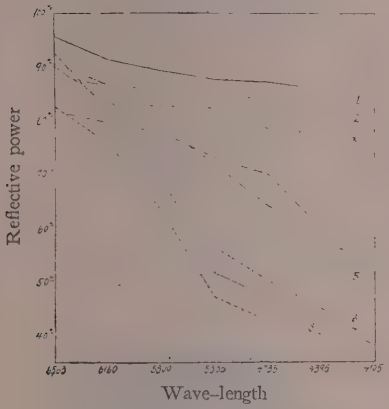


Fig. 9.

System of Ag–Cu

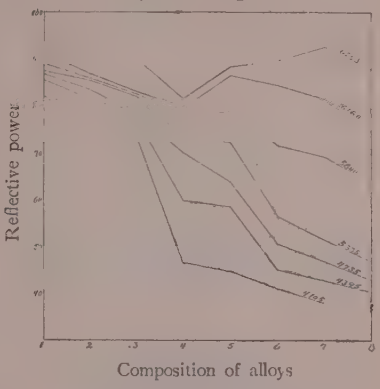
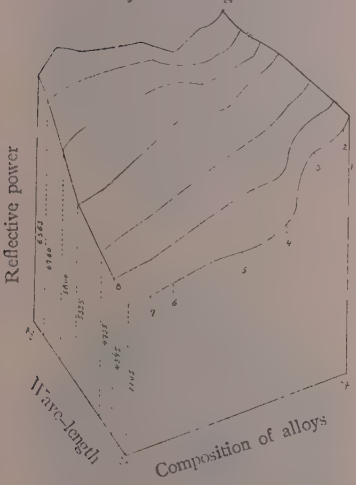


Fig. 10.

System of Ag–Cu



in Fig. 10. From these graphs, it is obvious that there exists a minimum point of reflective power between the wave-lengths 6563–5800 Å at the point corresponding to the eutectic. With wave-lengths shorter than 5800 Å, there is however no such minimum. The reason may be enunciated as follows :– Since the reflective power of pure copper decreases rapidly in the range of wave-lengths shorter than 5800 Å, that of the alloys having primary crystals of copper would be greatly influenced by the decreasing effect in the range of the shorter wave-lengths, as the result of which there would naturally be no minimum point observable at the eutectic point.

Whether the size of a crystal would have the same effect on the reflective power seemed necessary to be determined. The eutectic and 7 % Cu–alloys were tested for this purpose. In order to have the differences in the constituent crystal size made obvious, these alloys were

treated in two ways, furnace-cooled and annealed; the following is the specification of the samples:—

Table XX

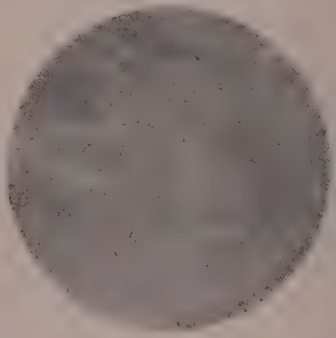
Samples	Kinds of alloys	Heat treatment
i	eutectic	furnace cooled
j	〃	annealed at 650° for 10 hours
k	7% Cu	furnace cooled
l	〃	annealed at 650° for 10 hours

The polished surfaces of each sample were etched with a 5% solution of ferric chloride and examined microscopically.

Fig. 11.

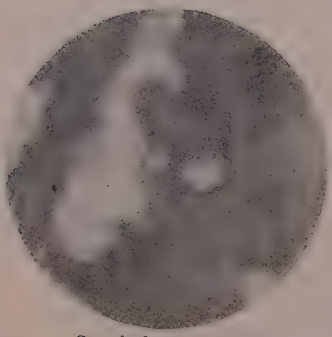
Sample i ×390

Fig. 12.



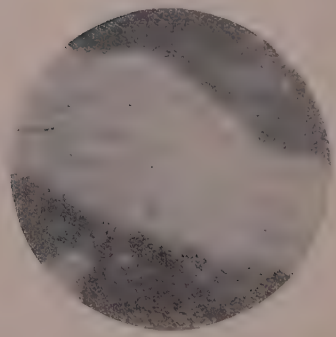
Sample j ×390

Fig. 13.



Sample k ×390

Fig. 14.



Sample l ×390

The samples, furnace cooled, i and k, had much smaller crystals than the annealed j and l, as may be seen from the photographs, Figs. 11, 12, 13 and 14. The results of determination are given in Table XXI for each sample and summarized in Table XXII. From these results, we may conclude that the difference in size of crystals have no much effect on the reflection,

Table XXI

Sample i

Wave-length	6563	6160	5800	5535	4735	4395
Photometric reading with direct exposure	53·8	53·25	53·1	51·6	45·3	57·2
Aperture of the sector deduced from Fig. 4.	111·48	109·70	109·28	104·84	85·69	123·06
Position on the "Wedge"	4	4	4	4	4	4
Photometric reading of the sample	61·2	57·9	55·8	49·75	41·3	41·8
Aperture of the sector deduced from Fig. 4.	137·40	125·16	117·94	98·86	73·67	75·10
Position on the "Wedge"	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66 87	66·87	66·87
Reflective power after two-fold reflection	67·15	63·54	60·41	53·43	49·12	35·96
Reflective power	81·95	79·72	77·73	73·10	70·09	59·97

Sample j

Wave-length	6563	6160	5800	5335	4735	4395
Photometric reading with direct exposure	53·8	53·25	53·1	51·6	45·3	57·2
Aperture of the sector deduced from Fig. 4.	111·48	109·70	109·28	104·84	85·69	123·06
Position on the "Wedge"	4	4	4	4	4	4
Photometric reading of the sample	60·5	57·9	56·0	49·9	41·35	41·75
Aperture of the sector deduced from Fig. 4.	134·83	125·16	118·72	99·43	73·83	74·99
Position on the "Wedge"	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	67·02	63·54	60·77	53·71	49·22	35·91
Reflective power	81·87	79·72	77·96	73·29	70·16	59·93

Sample k

Wave-length	6563	6160	5800	5335	4735	4395
Photometric reading with direct exposure	41·0	53·25	53·1	51·6	45·3	57·2
Aperture of the sector deduced from Fig. 4.	72·81	109·70	109·28	104·84	85·69	123·06
Position on the "Wedge"	4	4	4	4	4	4
Photometric reading of the sample	61·15	62·35	62·0	60·4	50·3	61·6
Aperture of the sector deduced from Fig. 4.	137·36	143·22	140·81	134·31	101·88	139·25
Position on the "Wedge"	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	81·79	71·84	70·98	70·61	65·97	63·07
Reflective power	90·44	84·76	84·25	84·03	81·24	79·42

Sample l

Wave-length	6563	6160	5800	5335	4735	4395
Photometric reading with direct exposure	41·0	53·25	53·1	51·6	45·3	57·2
Aperture of the sector deduced from Fig. 4.	72·91	109·70	109·28	104·84	85·69	123·06
Position on the "Wedge"	4	4	4	4	4	4
Photometric reading of the sample	61·2	62·5	62·0	60·3	50·8	61·6
Aperture of the sector deduced from Fig. 4.	137·39	144·04	140·81	134·10	102·07	139·25
Position on the "Wedge"	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	81·92	72·21	70·98	70·51	66·08	63·07
Reflective power	90·51	84·98	84·25	83·97	81·29	79·42

Table XXII

Reflective Power

Wave-length	6563	6160	5800	5335	4735	4395	4105
Sample d[1]	81·80%	79·66%	77·86%	73·21%	70·05%	59·97%	—
" i	81·95%	79·72%	77·73%	73·10%	70·09%	59·97%	—
" j	81·87%	79·72%	77·96%	73·29%	70·16%	59·93%	—
" k	90·44%	84·76%	84·25%	84·03%	81·24%	79·42%	—
" l	90·51%	84·98%	84·25%	83·97%	81·29%	79·42%	—

1 Sample d, which was annealed for 3 hours at 650°, is here cited in comparison with the others.

(2) The System of Copper and Cadmium

For materials, electrolytic copper and Merck's stick cadmium were used, the latter of which had the following purity :—

Table XXIII

Metal	Cd	Pb	Fe	Zn
%	99·20	0·66	0·09	trace

In accordance with Sahmen's state-diagram[1], the following samples were prepared :—

Table XXIV
Composition of the Samples

Samples	a	b	c	d	e	f	g
Percentage of Cadmium	100	99·5	98·89	95·0	90·0	80·0	72·35
Percentage of Copper	0	0·5	1·11	5·0	10·0	20·0	27·65

They were furnace cooled and annealed for one hour at a temperature 50° lower than the eutectic or the melting-temperatures according to the case. A vertical section of each sample in the middle was polished and subjected to determination exactly in the same manner as in the former system. The photogram of the reflected light is given in Fig. 15, and numerical data in Table XXVI and summarized in Table XXV.

Fig. 15.

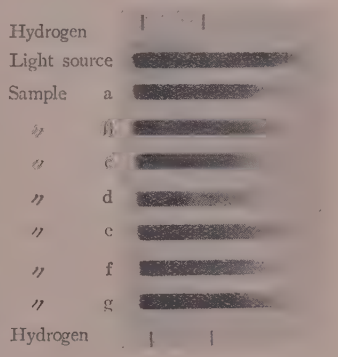


Table XXV
The reflective power of the system of copper and cadmium

Wave-length	6563	6160	5800	5335	4735	4395	4105
Sample a	83·95%	85·92%	84·15%	84·75%	86·18%	85·34%	82·18%
〃 b	80·04%	81·60%	80·24%	79·44%	78·40%	78·05%	77·41%
〃 c	68·73%	69·56%	69·49%	67·05%	66·82%	66·69%	66·37%
〃 d	71·84%	71·99%	73·37%	70·50%	69·39%	69·11%	68·54%
〃 e	72·92%	73·26%	74·21%	72·78%	72·45%	72·18%	71·83%
〃 f	76·25%	77·46%	79·04%	76·19%	73·66%	72·72%	72·11%
〃 g	75·18%	76·27%	78·67%	75·95%	71·88%	67·76%	61·69%

1 Zeit. f. Anorg. Chemie **49** 301 (1906).

Table XXVI

Sample a

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	52·7	51·0	52·1	51·7	47·3	43·0	54·2
Aperture of the sector deduced from Fig. 4.	108.04	102.40	106.56	105.18	92.17	78.88	112.72
Position on the "Wedge"	4	4	4	4	4	4	4
Photometric reading of the sample	61·4	61·25	61·0	61·4	56·7	51·5	61·3
Aperture of the sector deduced from Fig. 4.	138.11	137.74	136.88	137.26	121.82	104.53	137.45
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	66.87	66.87	66.87	66.87	66.87	66.87	66.87
Reflective power after two-fold reflection	70·47	73·81	70·78	71·82	72·64	72·82	67·52
Reflective power	83·95	85·92	84·15	84·75	86·18	85·34	82·18

Sample b

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	56·3	55·1	56·2	51·7	46·3	43·0	54·2
Aperture of the sector deduced from Fig. 4.	120.04	115.40	119.56	105.18	92.17	78.88	112.72
Position on the "Wedge"	4	4	4	4	4	4	4
Photometric reading of the sample	61·4	61·4	61·1	56·2	50·3	45·3	56·4
Aperture of the sector deduced from Fig. 4.	138.18	138.60	138.07	119.10	101.38	85.90	120.57
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	66.87	66.87	66.87	66.87	66.87	66.87	66 87
Reflective power after two-fold reflection	64·06	66·58	64·38	63·11	61·46	60·91	59·92
Reflective power	80·04	81·60	89·24	79·44	78·40	78·05	77·41

Sample c

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	56·3	55·1	56·2	51·7	47·3	43·0	54·2
Aperture of the sector deduced from Fig. 4.	120.04	115.40	119.56	105.18	92.17	78.88	112.72
Position on thd "Wedge"	4	4	4	4	4	4	4
Photometric reading of the sample	49·75	49·3	50·5	44·1	40·4	36·3	45·4
Aperture of the sector deduced from Fig. 4.	98.85	97.60	100.87	82.03	71.36	60.80	85.95
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	66.87	66.87	66.87	66.87	66.87	66.87	66.87
Reflective power after two-fold reflection	47·23	48·39	48·28	44·95	44·65	44·47	44·04
Reflective power	68·73	69·56	69·49	67·05	66·82	66·69	66·37

Sample d

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	56·3	55·1	56·2	51·7	47·3	43·0	54·2
Aperture of the sector deduced from Fig. 4.	120·04	115·40	119·56	105·18	92·17	78·88	112·72
Position on the "Wedge"	4	4	4	4	4	4	4
Photometric reading of the sample	52·9	51·7	53·6	47·1	42·6	38·2	47·35
Aperture of the sector deduced from Fig. 4.	108·69	105·27	110·82	91·61	77·53	65·74	92·26
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	51·60	51·83	53·82	49·70	48·15	47·75	46·97
Reflective power	71·84	71·99	73·37	70·50	69·39	69·11	68·54

Sample e

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	53·0	49·8	57·6	51·3	44·1	36·3	55·1
Aperture of the sector deduced from Fig. 4.	109·00	100·41	124·24	103·74	82·11	60·81	115·40
Position on the "Wedge"	4	4	4	4	4	4	4
Photometric reading of the sample	50·9	48·4	56·6	49·2	42·8	34·1	50·9
Aperture of the sector deduced from Fig. 4.	102·24	95·14	121·10	97·19	77·70	55·77	102·31
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	53·17	53·66	55·06	53·11	52·49	52·09	51·59
Reflective power	72·92	73·26	74·21	72·78	72·45	72·18	71·83

Sample f

Wave length	6563	6160	5800	5335	4735	4395	4150
Photometric reading with direct exposure	53·0	49·8	57·6	51·3	44·1	36·3	55·1
Apertute of the sector deduced from Fig. 4.	109·00	100·41	124·24	103·74	82·11	60·81	115·40
Position on the "Wedge"	4	4	4	4	4	4	4
Photometric reading of the sample	54·2	52·5	61·6	52·4	42·9	32·1	51·2
Aperture of the sector deduced from Fig. 4.	112·77	107·54	139·13	107·14	78·74	56·70	103·23
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	58·13	59·99	62·47	58·04	54·25	52·88	52·00
Reflective power	76·25	77·46	79·04	76·19	73·66	72·72	72·11

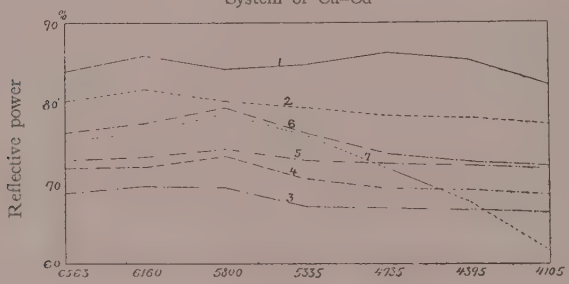
Sample g

Wave--length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	53·0	49·8	57·6	51·3	44·1	42·0	55·1
Aperture of the sector deduced from Fig. 4.	109.00	100.41	124.24	103.74	82.11	75.68	115.40
Position on the "Wedge"	4	4	4	4	4	4	4
Photometric reading of the sample	53·1	51·3	61·2	52·1	41·6	36·1	40·6
Aperture of the sector deduced from Fig. 4.	109.34	103.94	137.68	106.41	74.63	60.30	73.21
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	66.87	66.87	66.87	66.87	66.87	66.87	66.87
Reflective power after two-fold reflection	56·52	58·16	61·88	57·68	51·67	45·84	38·04
Reflective power	75·18	76·27	78·67	75·95	71·88	67·76	61.69

The relation between the reflective powers and wave lengths as well as that between the reflective powers and the compositions of the

Fig. 16.

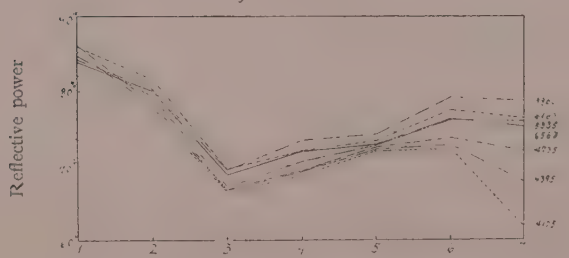
System of Cu–Cd



Wave length

Fig. 17

System of Cu–Cd

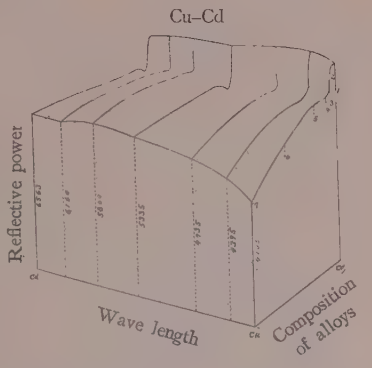


Composition of alloys

alloys are represented in Figs. 16 and 17 respectively, while the three dimensional relations between reflective powers, wave lengths and compositions of the alloys are represented in Fig. 18.

These Figures point to the minimum points of the reflective powers of all kinds of wave lengths situated in the position of the eutectic.

Fig. 18.



(3) The System of Tin and Cadmium.

The cadmium used was the same material as before, while the tin was of the following purity :—

Table XXVII

Metal	Sn	Fe	Pb	As and Sb
%	99·89	0·01	0·03	trace

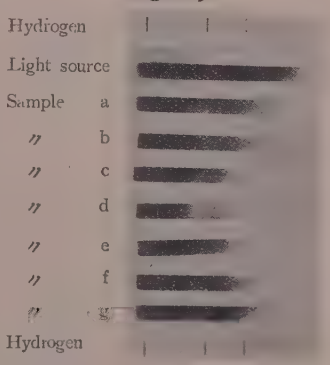
The samples were selected according to Schleicher's state-diagram[1] in the following way :—

Table XXVIII
Composition of the samples

Samples	a	b	c	d	e	f	g
Percentage of tin	0	15	35	68·7	85	93	100
Percentage of Cadmium	100	85	65	31·3	15	7	0

They were completely polished so as to have an optical plane as described in Paragraph 3. The photograms of the reflected light are given in Fig. 19. The numerical data are given in Table XXIX and summarized in Table XXX.

Fig. 19.



1 Intern. Zeits. Metallogr. **2**, 76 (1912).

Table XXIX.

Sample a

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	52·7	51·0	52·1	51·7	47·3	43·0	54·2
Aperture of the sector deduced from Fig. 4.	108·04	102·40	106·56	105·18	92·18	78·88	112·72
Position on the "Wedge"	4	4	4	4	4	4	4
Photometric reading of the sample	61·4	61·25	61·0	61·4	56·7	51·5	61·3
Aperture of the sector deduced from Fig. 4.	138·11	137·74	136·88	137·26	121·82	104·53	137·45
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	70·47	73·81	70·78	71·82	72·64	72·82	67·52
Reflective power	83·95	85·90	84·15	84·75	86·18	85·34	82·18

Sample b

Wave-length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with derect exposure	42·9	47·7	51·5	51·8	58·7	62·9	60·4
Aperture of the sector deduced from Fig. 4.	78·52	93·20	104·50	105·52	127·98	145·00	134·50
Position on the "Wedge"	2	2	2	2	2	2	2
Photometric reading of the sample	58·8	56·1	56·2	43·5	56·2	62·5	55·3
Apetrure of the sector deduced from Fig. 4.	128·33	119·25	119·54	80·34	119·51	144·35	116·12
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	43·86	43·86	43·86	43·86	43·86	43·86	43·86
Reflective power after two-fold reflection	59·98	44·74	43·38	29·95	32·49	38·23	33·59
Reflective power	77·45	66·89	65·86	63·21	57·00	61·83	57·96

Sample c

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	56·2	51·8	48·5	48·7	49·6	51·4	51·5
Aperture of the sector deduced from Fig. 4.	119·56	105·52	95·28	95·59	98·45	104·12	104·50
Position on the "Wedge"	2	III	III	III	III	III	III
Photometric reading of the sample	32·1	58·1	44·7	49·0	45·9	49·0	47·3
Aperture of the sector deduced from Fig. 4.	50·89	125·82	83·81	96·85	86·68	96·68	92·10
Position on the "Wedge"	7	VII	VII	VII	VII	VII	VII
Ratio of absorption	43·86	14·75	14·75	14·75	14·75	14·75	14·75
Reflective power after two-fold reflection	17·64	16·71	13·36	14·40	10·40	11·75	10·34
Reflective power	42·00	40·87	35·16	37·97	31·74	34·28	32·16

Sample d

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	50·2	62·3	51·8	59·7	60·1	56·6	61·6
Aperture of the sector deduced from Fig. 4.	100·12	142·88	105·52	131·88	133·30	121·30	139·14
Position on the "Wedge"	III	III	III	III	III	III	III
Photometric reading of the sample	47·5	58·6	38·5	38·7	30·6	37·9	35·4
Aperture of the sector deduced from Fig. 4.	92·72	127·73	66·33	66·89	46·34	65·01	58·65
Position on the "Wedge"	VII	VII	VII	VII	VII	VII	VII
Ratio of absorption	14·75	14·75	14·75	14·75	14·75	14·75	14·75
Reflective power after two-fold reflection	12·07	12·86	75·87	62·40	44·25	65·63	52·76
Reflective power	34·87	35·86	27·52	24·98	21·04	25·62	22·97

Sample e

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	51·1	62·1	55·6	62·2	61·7	51·4	51·5
Aperture of the sector deduced from Fig. 4.	102·98	141·56	117·82	142·22	139·54	104·12	104·50
Position on the "Wedge"	2	2	III	2	2	III	III
Photometric reading of the sample	29·6	45·0	54·2	26·3	29·3	47·7	46·8
Aperture of the sector deduced from Fig. 4.	42·72	84·78	112·75	41·50	41·16	93·13	90·86
Position on the "Wedge"	7	7	VII	7	7	VII	VII
Ratio of absorption	43·86	43·86	14·75	43·86	43·86	13·75	14·75
Reflective power after two-fold reflection	17·23	24·07	13·96	11·68	10·15	11·06	96·28
Reflective power	41·52	49·07	37·77	34·18	31·87	33·26	31·03

Sample f

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	51·5	62·1	55·6	62·2	61·7	51·4	51·5
Aperture of the sector deduced from Fig. 4.	102·98	141·56	117·82	142·22	139·54	104·12	104·50
Position on the "Wedge"	2	2	2	2	2	III	III
Photometric reading of the sample	44·9	63·0	42·6	30·1	29·6	49·7	48·9
Aperture of the sector deduced from Fig. 4.	84·29	145·35	77·41	44·50	42·89	99·49	96·42
Position on the "Wedge"	7	7	7	7	7	VII	VII
Ratio of absorption	43·86	43·86	43·86	43·86	43·36	14·75	14·75
Reflective power after two-fold reflection	31·99	39·00	26·20	23·43	11·31	13·66	11·79
Reflective power	56·57	62·69	51·19	35·26	33·63	36·97	34·35

Sample g

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	51·0	42·6	55·0	57·4	57·0	61·6	60·4
Aperture of the sector deduced from Fig. 4.	192·98	77·45	115·00	123·62	122·50	139·14	134·50
Position on the "Wedge"	III	2	III	II	2	2	2
Photometric reading of the sample	29.6	59·0	37·5	33·3	50·8	61·4	56·9
Aperture of the sector deduced from Fig. 4.	43·92	128·84	63·81	53·95	102·35	138·52	122·32
Position on the "Wedge"	VII	7	VII	VII	7	7	7
Ratio of absorption	14·75	43·86	14·75	12·18	43·86	43·86	43·86
Reflective power after two-fold reflection	53·49	61·00	50·28	45·59	32·60	38·23	35·21
Reflective power	73·14	78·10	70·91	67·52	57·10	61·81	59·34

Table XXX

The Reflective Power of the System of Cadmium and Tin.

Wave length		6563	6160	5800	5335	4735	4395	4105
Sample	a	83·95%	85·90%	84·15%	84·75%	86·18%	85·34%	82·18%
〃	b	77·45%	66·89%	65·86%	63·21%	57·00%	61·83%	57·96%
〃	c	42·00%	40·87%	35·16%	37·97%	31·74%	34·28%	32·16%
〃	d	34·87%	35·86%	27·52%	24·98%	21·04%	25·62%	22·97%
〃	e	41·52%	49·07%	37·77%	34·18%	31·87%	33·26%	31·03%
〃	f	56·57%	62·69%	51·19%	35·26%	33·63%	36·97%	34·35%
〃	g	73·14%	78·10%	70·91%	67·52%	57·10%	61·81%	59·34%

The relation between the reflective powers and wave lengths as well as that between the reflective powers and the compositions of the

Fig. 20.

System of Cd–Sn

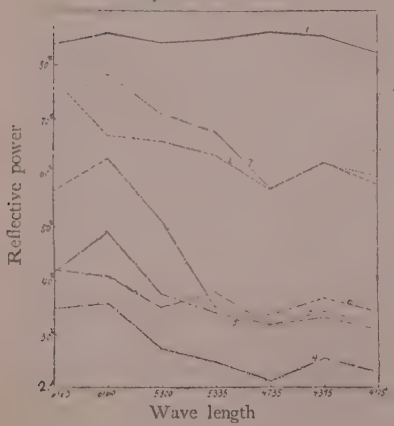
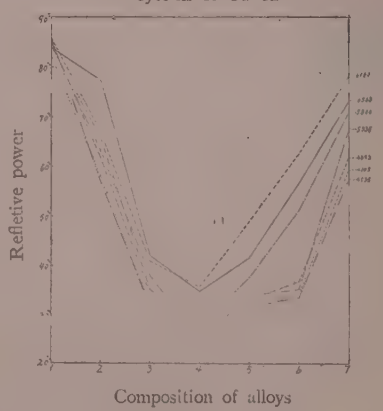


Fig. 21.

System of Cd–Sn

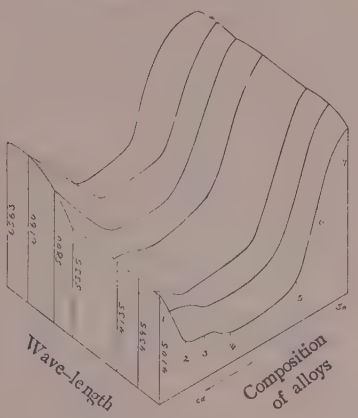


alloys are as represented in Figs. 20 and 21 respectively, while the three dimensional relations between reflective powers, wave lengths and compositions of the alloys are as represented in Fig. 22.

The minimum point of the reflected powers for any wave length is here also found to be in the position of the eutectic.

Fig. 22.

System of Cd–Sn



(4) The System of Bismuth and Cadmium.

The cadmium used was the same as before, and the bismuth of the purity of 99.25%, the remainder being 0·20% Ag and 0·61% Mn. The

Table XXXI

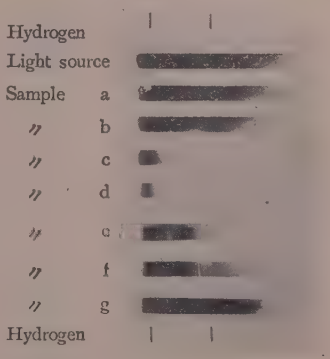
The Composition of the Samples

No. of Samples	a	b	c	d	e	f	g
Percentage of Cadmium	100	81	62	40	26	13	0
Percentage of Bismuth	0	19	38	60	74	87	100

samples were selected, according to Petrenko and Fedorow's state-diagram[1], as in Table XXXI and polished to an optical plane. In order to avoid oxidation, the samples were polished with rouge on a pitch plate wetted with absolute alcohol, washed with ether and quickly dried.

The photograms of the spectra are given in Fig. 23 and the results of determination are given in Table XXXII and summarized in Table XXXIII.

Fig. 23.



1 Intern. Zeits. Metallogr. **6**, 212 (1914).

Table XXXII

Sample a

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	52·7	51·0	52·1	51·7	47·3	43·0	54·2
Aperture of the sector deduced from Fig. 4.	108·04	102·40	106·56	105·18	92·18	78·88	112·72
Position on the "Wedge"	4	4	4	4	4	4	4
Photometric reading of the sample	61·4	61·25	61·0	61·4	56·7	51·5	61·3
Aperture of the sector deduced from Fig. 4.	138·11	137·74	136·88	137·26	121·82	104·53	137·45
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	66·87	66·87	66·87	66·87	66·87	66·87	66·87
Reflective power after two-fold reflection	70·47	73·81	70·78	71·82	72·64	72·82	67·52
Reflective power	83·95	85·90	84·15	84·75	86·18	85·34	82·18

Sample b

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading withdirect exposure	49·1	55·6	49·0	49·0	45·0	46·7	45·4
Aperture of the sector deduced from Fig. 4.	97·10	51·88	96·83	96·83	84·72	90·41	85·93
Position on the "Wedge"	2	2	2	2	2	2	2
Photometric reading of the sample	52·3	31·2	40·8	50·5	58·3	61·3	61·1
Aperture of the sector deduced from Fig. 4.	107·12	48·40	72·52	101·05	126·61	137·54	137·12
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	43·86	43·86	43·86	43·86	43·86	43·86	43·86
Reflective power after two-fold reflection	41·99	36·03	25·51	39·91	55·33	69·33	58·75
Reflective power	64·79	60·03	54·33	69·43	74·39	79·95	76·65

Sample c

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	62·3	60·1	61·0	56·5	58·6	61·4	58·4
Aperture of the sector deduced from Fig. 4.	142·88	133·30	136·80	121·04	127·60	138·32	126·96
Position on the "Wedge"	III	II	2	2	II	III	II
Photometric reading of the sample	57·7	49·5	44·6	54·0	34·5	35·5	31·3
Aperture of the sector deduced from Fig. 4.	124·75	99·24	83·37	111·94	56·85	77·00	49·00
Position on the "Wedge"	VII	VII	7	7	VII	VII	VII
Ratio of absorption	14·75	12·18	43·86	43·86	12·18	14·75	12·18
Reflective power after two-fold reflection	99·22	74·09	30·17	32·25	46·44	53·20	40·76
Reflective power	31·50	27·22	17·37	17·96	21·55	23·07	20·19

Sample d

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	62·3	60·1	55·6	58·4	59·0	61·4	58·0
Aperture of the sector deduced from Fig. 4.	142·88	133·30	117·32	126·96	128·85	138·32	125·60
Position on the "Wedge"	III	II	2	2	2	III	2
Photometric reading of the sample	57·0	61·5	33·3	35·7	53·2	45·1	50·0
Aperture of the sector deduced from Fig. 4.	122·60	138·95	54·20	59·21	109·41	85·08	99·59
Position on the "Wedge"	VII	VII	7	7	7	VII	7
Ratio of absorption	14·75	12·18	43·86	43·86	43·86	14·75	43·86
Reflective power after two-fold reflection	84·73	48·22	19·01	19·20	33·08	46·85	31·08
Reflective power	29·11	21·96	13·79	13·86	18·19	21·40	17·63

Sample e

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	62·3	62·5	61·6	57·0	58·6	61·4	58·4
Aperture of the sector deduced from Fig. 4.	142·88	144·20	139·14	122·50	127·60	138·32	126·96
Position on the "Wedge"	III	III	II	II	II	III	II
Photometric reading of the sample	59·6	57·8	32·2	30·2	41·2	39·2	33·8
Aperture of the sector deduced from Fig. 4.	162·26	124·90	51·17	45·21	73·43	68·37	55·27
Position on the "Wedge"	VII	VII	VII	VII	VII	VII	VII
Ratio of absorption	14·75	14·75	12·18	12·18	12·18	14·75	12·8
Reflective power after two-fold reflection	11·74	93·33	39·08	39·12	58·61	60·66	45·45
Reflective power	34·27	30·55	19·77	19·78	24·21	24·96	21·32

Sample f

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	62·3	62·5	61·6	57·0	62·1	61·4	60·5
Aperture of the sector deduced from Fig. 4.	142·88	144·20	139·14	122·50	141·58	138·32	134·90
Position on the "Wedge"	III	III	II	II	III	III	III
Photometric reading of the sample	32·8	57·6	38·1	36·7	59·2	57·6	55·4
Aperture of the sector deduced from Fig. 4.	52·83	124·40	65·31	61·75	129·70	124·34	11·62
Position on the "Wedge"	VII	VII	VII	VII	VII	VII	VII
Ratio of absorption	14·75	14·75	12·18	12·18	14·75	14·75	14·75
Reflective power after two-fold reflection	12·25	97·71	48·70	51·98	11·41	10·69	91·62
Reflective power	35·00	31·26	22·07	22·80	33·78	34·86	30·27

Sample g.

Wave length	6963	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	60.6	58.6	62.2	39.8	52.1	55.8	55.7
Aperture of the sector deduced from Fig. 4.	135.28	127.60	142.22	69.95	106.44	117.96	117.64
Position on the "Wedge"	2	2	2	2	2	2	2
Photometric reading of the sample	59.1	47.0	35.2	30.5	32.5	53.2	46.4
Aperture of the sector deduced from Fig. 4.	129.53	91.33	59.33	46.08	51.89	109.64	89.52
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	43.86	43.86	43.86	43.86	43.86	43.86	43.86
Reflective power after two-fold reflection	36.89	28.31	17.07	26.26	19.96	35.88	29.94
Reflective power	60.75	52.31	53.48	51.25	44.68	59.91	54.72

Table XXXIII

The reflective power of the system of bismuth and cadmium

Wave lemgh		6563	6160	5800	5335	4735	4395	4105
Sample	a	83.95%	85.90%	84.15%	84.75%	86.18%	85.34%	82.18%
〃	b	64.95%	60.03%	54.33%	69.43%	74.39%	79.95%	76.65%
〃	c	31.50%	27.22%	17.37%	17.96%	21.55%	23.07%	20.19%
〃	d	29.11%	21.96%	13.79%	13.86%	18.19%	21.40%	17.63%
〃	e	34.27%	30.55%	19.77%	19.78%	24.21%	24.69%	21.32%
〃	f	35.00%	31.26%	22.07%	22.80%	33.73%	34.86%	30.27%
〃	g	60.75%	52.31%	53.48%	51.25%	44.68%	55.91%	54.72%

Fig. 24.

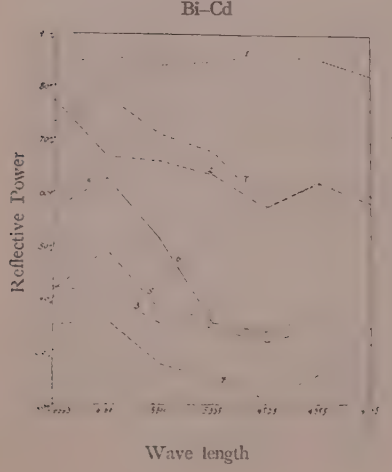
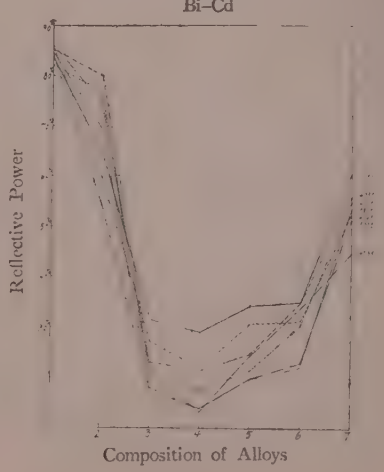
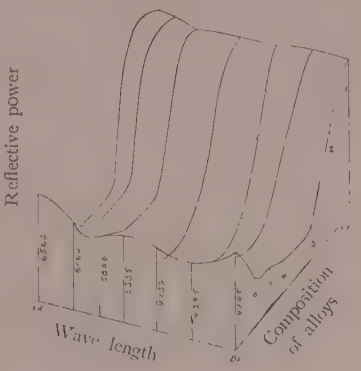


Fig. 25.



The relation between the reflective powers and the wave lengths, as well as that between the reflective powers and the compositions are as represented in Figs. 24 and 25 respectively, while the three dimensional relations between the reflective powers, wave lengths and compositions are represented in Fig. 26. The minimum points of reflected powers for all kinds of wave lengths are also found to be at the eutectic point.

Fig. 26.



(5) The System of Bismuth and Tin.

The samples were selected according to Guertler's state-diagram[1] and polished to an optical plane. They had the following composition :—

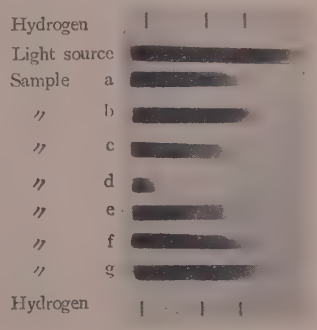
Table XXXIV

Composition of the sample

No. of Samples	a	b	c	d	e	f	g
Percentage of Tin	0	13	27	42	62	81	100
Percentage of Bismuth	100	87	73	58	38	19	0

The photograms of the reflected light are given in Fig. 27, and the numerical data in Table XXXV and summarized in Table XXXVI.

Fig. 27.



The relation between the reflective powers and the wave lengths, as well as that between the reflective powers and the compositions are represented in Figs. 28 and 29 respectively, while the three dimensional relations between the reflective powers, wave-lengths and compositions are represented in Fig. 30. The minimum points of the reflected powersfor all kinds of wave lengths are here also found at the eutectic point.

1 Guertler, Metallographie I, 738 (1912).

Table XXXV

Sample a

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	60.6	28.6	62.2	39.8	52.1	55.8	55.7
Aperture of the sector deduced from Fig. 4.	135.28	127.60	142.22	69.95	106.44	117.96	117.64
Position on the "Wedge"	2	2	2	2	2	2	2
Photometric reading of the sample	59.1	47.0	35.2	30.5	32.5	53.2	46.4
Aperture of the sector deduced from Fig. 4.	129.53	91.33	59.33	46.08	51.89	109.64	89.52
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	43.86	43.86	43.86	43.86	43.86	43.86	43.86
Reflective power after two-fold reflection	36.89	28.31	17.07	26.26	19.96	35.88	29.94
Reflective power	60.75	52.31	53.48	51.25	44.68	59.91	54.72

Sample b

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	58.6	51.1	44.0	46.9	46.3	37.2	52.5
Aperture of the sector deduced from Fig. 4.	127.60	102.98	81.85	91.08	89.09	62.98	107.4
Position on the "Wedge"	III	III	III	III	III	III	2
Photometric reading of the sample	61.8	58.6	55.2	48.7	57.1	53.5	33.4
Aperture of the sector deduced from Fig. 4.	139.84	127.62	115.76	95.92	122.73	111.92	54.18
Position on the "Wedge"	VII	VII	VII	VII	VII	VII	7
Ratio of absorption	14.75	14.75	14.75	14.75	14.75	14.75	43.86
Reflective power after two-fold reflection	15.48	17.30	19.52	14.93	19.03	24.02	20.06
Reflective Power	39.35	41.60	44.19	38.64	43.63	49.02	44.79

Sample c

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	58.6	58.0	61.7	46.9	46.3	37.2	53.4
Aperture of the sector deduced frhm Fig. 4.	127.60	125.60	139.28	156.02	89.09	62.98	110.12
Position oo the "Wedge"	III	III	III	III	III	III	III
Photometric reading of the sample	60.6	59.4	61.2	43.0	52.0	50.5	62.1
Aperture of the sector deduced from Fig. 4.	135.43	130.69	137.74	78.74	106.3	101.01	141.75
Position on the "Wedge"	VII	VII	VII	VII	VII	VII	VII
Ratio of absorption	14.75	14.75	14.75	14.75	14.75	14.75	12.18
Reflective power after two-fold reflection	15.03	14.79	14.08	11.68	16.72	21.88	17.91
Reflective power	38.77	38.46	37.53	34.18	40.89	46.78	42.32

Sample d

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	62·4	54·3	53·1	60·0	62·5	56·6	61·7
Aperture of the sector deduced from Fig. 4.	143·54	112·98	109·28	132·90	144·20	121·30	139·28
Position on the "Wedge"	III	III	III	III	III	III	III
Photometric reading of the sample	58·1	49·8	34·6	43·9	59·4	58·8	57·0
Aperture of the sector deduced from Fig. 4.	125·91	98·42	56·98	81·53	130·82	188·22	122·45
Position on the "Wedge"	VII	VII	VII	VII	VII	VII	VII
Ratio of absorption	14·75	14·75	14·75	14·75	14·75	14·75	14·75
Reflective power after two-fold reflection	10·28	97·78	63·99	74·21	11·00	13·84	10·03
Reflective power	32·09	31·27	25·30	27·24	33·18	37·21	31·68

Sample e

Wave length	6563	6160	5800	5335	4735	4955	4105
Photometric reading with direct exposure	62·4	57·3	56·5	53·1	62·0	57·9	61·7
Aperture of the sector deduced from Fig. 4.	143·54	123·34	121·00	109·28	140·70	125·26	139·28
Position on the "Wedge"	2	III	III	III	III	III	III
Photometri reading of the sample	38·2	54·9	30·5	51·4	59·3	60·2	58·3
Aperture of the sector deduced from Fig. 4.	65·19	114·61	46·12	104·04	130·44	132·12	125·51
Position on the "Wedge"	7	VII	VII	VII	VII	VII	VII
Ratio of absorption	43·86	14·75	14·75	14·75	14·75	14·75	14·75
Reflective power after two-fold reflection	18·72	12·29	72·25	84·10	12·04	14·95	10·86
Reflective power	43·27	35·07	26·88	29·00	34·70	38·67	32·96

Sample f

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	60·6	58·6	62·2	56·6	56·6	55·8	55·7
Aperture of the sector deduced from Fig. 4.	135·28	127'60	142·22	121·30	121·30	117·96	117·64
Position on the "Wedge"	2	2	2	2	2	2	2
Photometric reading of the sample	48·6	37·0	3·25	35·3	39·3	50·9	45·9
Apertnre of the sector deduced from Fig. 4.	95·70	62·52	58·33	60·95	68·36	103·24	87·62
Position on the "Wedge"	7	7	7	7	7	7	7
Ratio of absorption	43·86	43·86	43·86	43·86	43·86	43'86	43·86
Reflective power after two-fold reflection	28·01	20·05	17·07	23·26	25·67	33·98	29·45
Reflective power	52·92	44·79	41·32	48·23	50·67	58·30	54·27

Sample g.

Wave length	6563	6160	5800	5335	4735	4395	4105
Photometric reading with direct exposure	51·0	42·6	55·0	57·4	57·0	61·6	60·4
Aperture of the sector deduced from Fig, 4.	102.98	77·45	115·00	123'62	112.62	139·14	134·50
Position on the "Wedge"	III	2	III	II	2	2	2
Photometric reading of the sample	29·6	59·0	37·5	33·3	50·8	61·4	56·9
Apeiture of the sector deducee from Fig· 4.	43·92	128·84	63·81	53·95	102·35	138·52	122·32
Position on the "Wedge"	VII	7	VII	VII	7	7	7
Ratio of absorption	14·75	43·86	14 75	12·18	43·86	43·86	43·86
Reflective power after two-fold reflectian	53·49	61·00	20·28	45·59	32·60	38·23	35·21
Reflection power	73·14	78·10	70·91	67·52	57·10	61·81	59·34

Table XXXVI.

The reflective power of the alloys of the System :—

Wave length		6563	6160	5800	5335	4735	4395	4105
Sample	a	60·75%	52·31%	53·48%	51·25%	44·68%	59·91%	54·72%
〃	b	39·35%	41·60%	44·19%	38·64%	43·63%	49·02%	44·79%
〃	c	38·77%	38·46%	37·53%	34·18%	40·89%	46·78%	42·32%
〃	d	32·09%	31·27%	25·30%	27·24%	33·18%	37·21%	31·68%
〃	e	43·27%	35·07%	26·88%	29·00%	34·70%	38·67%	32·96%
〃	f	52·92%	44·79%	41·32%	48·23%	56·67%	58·30%	54·27%
〃	g	73·14%	78·10%	70·91%	67·52%	57 10%	61·81%	59·34%

Fig. 28.

Bi–Sn

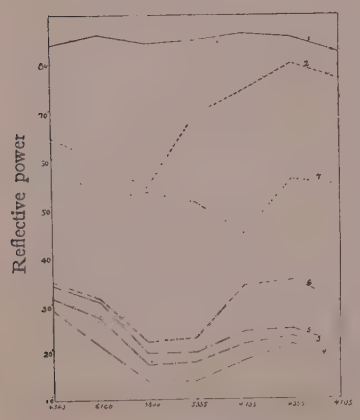


Fig. 29.

Bi-Sn

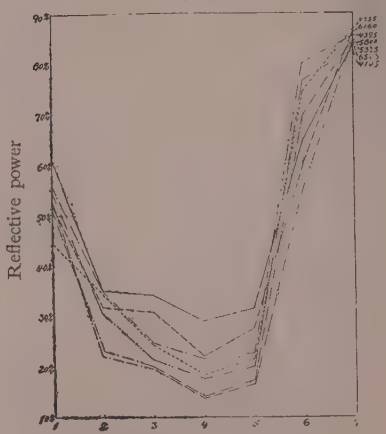


Fig. 30.

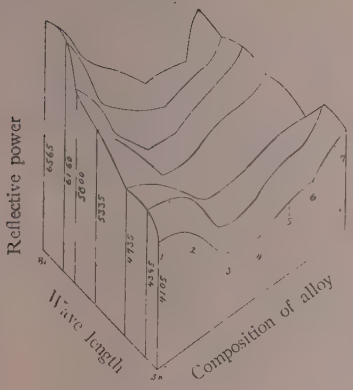


Fig. 31.

Pure tin

Fig. 32.

Alloy of
93% *Sn* and 7% *Cd*

Fig. 33.

Alloy of
85% *Sn* and 15% *Cd*

Fig. 34.

Eutectic alloy of
68·7% *Sn* and 31·3% *Cd*

VI Discussion of the Results.

The experiments have shown that the reflective power of the binary eutectic alloys has usually a minimum at the eutectic point, excepting the case where the reflective powers between 2 components are considerably different. In the latter case, as other workers have already shown[1], the minimum is liable to deviate to the side of the weaker component. As for the reason why the eutectic shows the minimum, one might consider that, the eutectic, being harder than any other alloy of the same components, is apt to get the more rough polish, in consequence of which the reflection is worse. This consideration is however not right. Our experiments with the alloys, *Bi–Sn*, *Sn–Cd* and *Cd–Bi*, which were each polished to an optical plane, showed actually not much difference in their reflective power in comparison with the alloys not optically plane. In fact, the optical plane of *Sn–Cd* had a reflective power only 3% higher, that of *Cd–Bi* 2·8%, and that of *Bi–Sn* 3·5%. These results indicate that the roughness of surface is not the real cause of the minimum reflection.

Another consideration is as follows :— the thickness of the lamella in the eutectic must, of course, be different in different alloys, but it may be probably assumed that it has in the average the order of Belaiew's determination[2]. The incident ray upon the surface of the eutectic must

1 Zeit. f, Anorg. Chemie **194**, 334 (1926).

2 Belaiew, Inst. Iron and Steel, 1922, 201, points out that the thickness of the cementite lamella in pearlite is in order of 75 μμ.

have, while transmitting some lamella, some part absorbed or scattered owing to the irregularity of the centre of diffraction. This absorption or scattering, due to the fine structure of the eutectic, might therefore be the principal cause of the low reflective power. As to the scattering effect, we present some photograms showing the image of the slit, through which pass the reflected rays from *Cd–Sn* alloys, in Figs. 31, 32, 33 and 34. The image of the eutectic gives there the largest opening owing to the strongest scattering effect.

The present study has been carried out under the kind suggestions and encouragement of Professor M. Chikashige to whom are due the investigator's cordial thanks.

The Quantitative Determination of the Degree of Tarnishing of a Metallic Surface by its Reflective Power.

By

Genmosuke Ando.

(Received December 16, 1927)

The polished surface of ordinary metals and alloys get tarnished if they are left open to the air, but for the degree of tarnishing there has been known no adequate method of measurement. Applying the principle of measuring the reflective power as described in my former paper,[1] I have devised a new method, which runs as follows :—

The samples, which have been measured for their reflective powers directly after polishing, are allowed to stand 24 hours in a special room containing specified quantities of moisture and carbon dioxide, and then again measured for their reflective powers now diminished. The ratio between both determinations gives the degree of tarnishing.

This method has been applied to the alloys of the systems, copper and silver, copper and cadmium, tin and cadmium, bismuth and cadmium, and bismuth and tin. The numerical data together with the graphs are given in the following pages :—

1 These memoirs, A, **11**, 43 (1928).

A. System of Copper and Silver

Table I

Reflective Power of the Alloys of Copper and Silver

a. Immediately after Polishing

No.	Sample Composition		Reflective power in % for wave length						
	Cu in %	Ag in %	6563	6160	5800	5335	4735	4395	4105
1	100	0	95·71	91·30	89·28	87·70	87·36	85·88	82·02
2	98	2	90·75	86·70	85·88	85·50	83·88	81·61	78·26
3	85	15	90·12	83·08	82·81	82·42	78·67	77·50	73·96
4	72	28	81·80	79·66	77·86	73·21	70·05	59·97	46·60
5	50	50	88·61	86·43	78·90	72·69	64·30	58·73	44·65
6	20	80	89·75	84·49	71·48	56·71	50·32	45·01	40·81
7	10	90	92·61	81·80	69·41	51·80	47·33	42·65	38·35
8	0	100	82·79	75·65	63·20	47·30	42·76	40·31	

b. After standing in a room at 14° C. with 4·8 % CO_2[1] by volume and 13·66 moisture[2] in terms of relative humidity

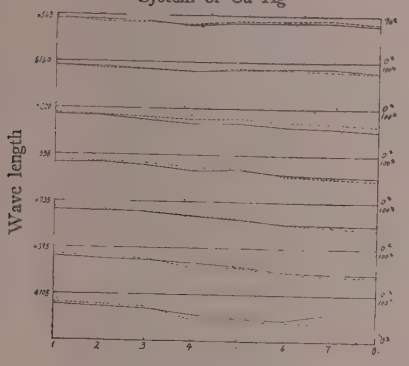
No.	Sample Composition		Reflective power in % for wave length						
	Cu in %	Ag in %	6563	6160	5800	5335	4735	4395	4105
1	100	0	91·03	91·57	85·81	82·42	81·09	81·24	77·38
2	98	2	90·13	90·01	84·31	84·32	80·00	77·70	74·17
3	85	15	89·08	85·60	75·10	77·52	76·06	74·81	70·53
4	72	28	79·80	81·35	67·60	66·17	68·28	68·86	57·90
5	50	50	85·60	83·83	68·57	68·10	63·32	60·48	48·44
6	20	80	85·00	87·73	60·95	58·47	52·61	17·44	45·84
7	10	90	86·06	87·07	58·70	55·78	52·02	46·89	42·78
8	0	100	73·36	79·05	52·30	53·12	50·10	45·24	

1 The determination of carbon dioxide was made from the decrease of the volume of the air after absorbing carbon dioxide in a caustic soda solution.: *vide* Scott's "Method of Air Analysis", 1912, p. 62.

2 The determination of moisture was made from the increase of the weight of a dry pumice-stone after passing a definite volume of air: Scott's "Method of Air Analysis", p. 95.

Fig. 1

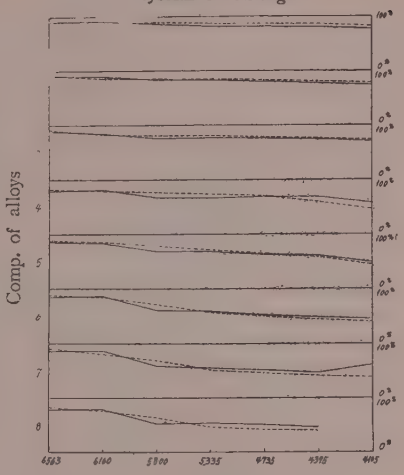
System of Cu-Ag



Reflective power after standing in *full* line.
Reflective power before standing in *dotted* line.

Fig. 2

System of Cu–Ag



Reflective power after standing in *full* line.
Reflective power before standing in *dotted* line.

B. System of Copper and Cadmium

Table III

Reflective Power of the Alloys of Copper and Cadmium.

a. Immediately after Polishing

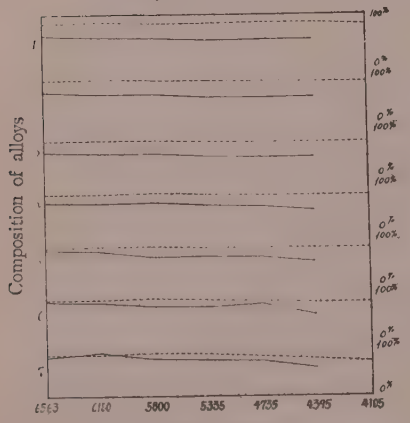
No.	Sample Composition		Reflective power in % for wave length						
	Cu in %	Cd in %	6563	6160	5800	5335	4735	4395	4105
1	0	100	83·95	85·92	84·15	84·75	86·18	85·34	82·18
2	0·5	99·5	80·04	81·60	80·24	79·44	78·40	78·05	77·41
3	1·1	98·9	68·73	69·56	69·49	67·05	66·82	66·69	66·37
4	5·0	95·0	71·84	71·99	73·37	70·50	69·39	69·11	68·54
5	10·0	90·0	72·92	73·26	74·21	72·78	72·45	72·18	71·83
6	20·0	80·0	76·25	77·46	79·04	76·19	73·66	72·72	72·11
7	27·7	72·3	75·18	76·27	78·67	75·95	71·88	67·76	61·69

b. After standing in a room at 14° C. with 4·8 % CO_2 by volume and 13·66 moisture in terms of relative humidity

No.	Sample Composition		Reflective power in % for wave length					
	Cu in %	Cd in %	6563	6160	5800	5335	4735	4395
1	0	100	60·17	58·76	57·02	53·28	54·29	54·69
2	0·5	99·5	59·00	54·69	54·92	49·92	48·18	48·28
3	1·1	98·9	48·32	45·93	46·97	40·69	37·36	38·59
4	5·0	95·0	55·30	54·69	56·70	50·29	48·17	42·34
5	10·0	60·0	69·95	66·41	55·43	67·41	55·84	46·94
6	20·0	80·0	74·04	72·37	65·42	64·40	68·17	48·55
7	27·4	72·3	72·96	79·29	68·60	66·79	64·06	50·82

Fig. 4

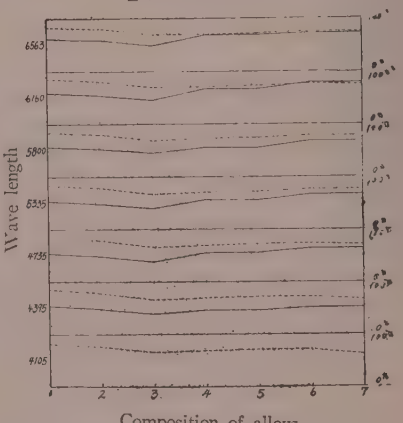
System of Cu–Cd



Reflective power after standing in *full* line.
Reflective power before standing in *dotted* line.

Fig. 3

System of Cu–Cd



Reflective power after standing in *full* line.
Reflective power before standing in *dotted* line.

C. System of Tin and Cadmium

Table V

Reflective Power of the Alloys of Tin and Cadmium

a. Immediately after Polishing

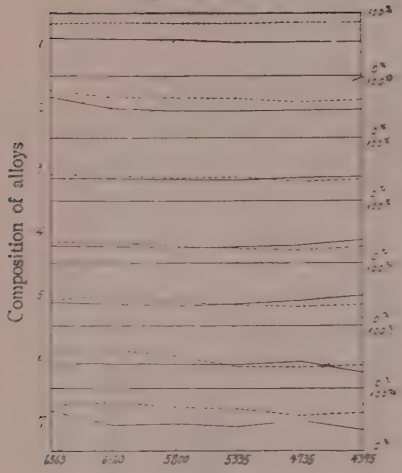
No.	Sample Composition		Reflective power in % for wave length						
	Sn in %	Cd in %	6563	6160	5800	5335	4735	4395	4105
1	0	100	83·95	85·92	84·15	84·75	86·18	85·34	82·18
2	15	85	77·45	66·89	65·86	63·21	57·00	61·83	57·96
3	35	65	42·00	40·87	35·16	37·97	31·74	34·28	32·16
4	68·7	31·3	23·87	35·86	27·52	24·98	21·04	25·62	22·97
5	85	15	41·52	49·07	37·77	34·18	31·87	33·26	31·03
6	93	7	56·57	62·69	51·19	35·26	33·63	36·97	34·35
7	100	0	73·14	78·10	70·91	67·52	57·10	61·81	59·34

b. After standing in a room at 26° C. with 3·4 % CO_2 and 76·19 moisture in terms of relative humidity

No.	Sample Composition		Reflective power in % for wave length					
	Sn in %	Cd in %	6563	6160	5800	5335	4735	4395
1	0	100	60·17	58·76	57·02	53·28	54·59	54·69
2	15	85	66·96	48·46	44·63	44·12	44·61	46·05
3	35	65	36·98	36·25	33·91	34·71	37·61	38·98
4	68·7	31·3	28·90	27·62	24·56	25·71	29·34	36·79
5	85	15	37·78	35·36	32·67	35·13	41·50	47·35
6	93	7	40·05	39·44	39·46	37·86	43·98	25·63
7	100	0	64·78	42·10	43·34	39·69	49·91	33·52

Fig. 6

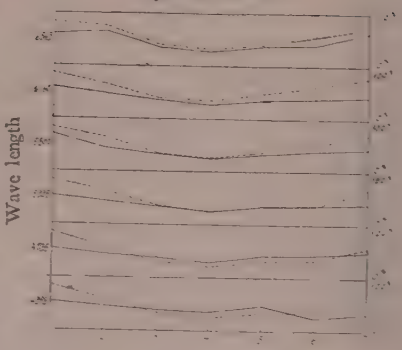
System of Cd–Sn



Reflective power after standing in *full* line.
Reflective power before standing in *dotted* line.

Fig. 5

System of Cd–Sn



Composition of alloys

Reflective power after standing in *full* line.
Reflective power before standing in *dotted* line.

D. System of Bismuth aud Cadmium.

Table VII

Reflective Power of the Alloys of Bismuth and Cadmium

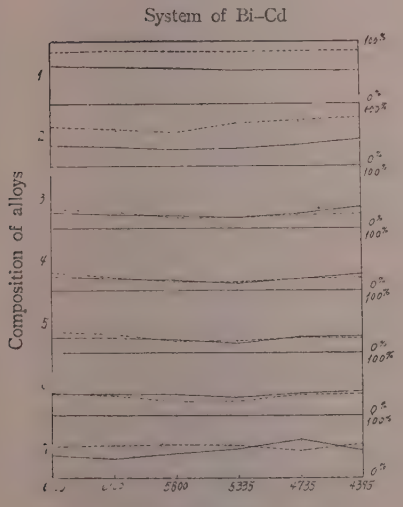
a. Immediately after Polishing

No.	Sample Composition		Reflective power in % for wave length						
	Cd in %	Bi in %	6563	6160	5800	5335	4738	4395	4105
1	100	0	83·95	85·92	84·15	84·75	86·18	85·34	82·18
2	81	19	64·79	60·03	54·33	69·43	74·39	79·95	76·65
3	62	38	31·50	27·22	17·37	17·96	21·55	23·07	20.19
4	40	60	29·11	21·96	13·79	13·86	18·19	21·40	17·63
5	26	74	34·27	30·55	19·78	19·78	24·21	24·69	21·32
6	13	87	35·00	31·26	22·07	22·80	33·73	34·86	30·27
7	0	100	60·75	52·31	53·48	51·25	44·68	55·91	54·72

b. After standing in a room at 26° C. with 3·4 % CO_2 and 76·19 moisture in terms of relative humidity

No.	Sample Composition		Reflective pawer in % for wave length					
	Cd in %	Bi in %	6563	6160	5800	5335	4735	4395
1	100	0	60·17	58·76	57·02	53·28	54·59	54·69
2	81	19	33·23	31·85	27·91	28·23	34·98	43·31
3	62	38	25·91	22·46	20·57	17·85	23·67	35·16
4	40	60	22·81	18·75	16·88	11·80	18·87	26·29
5	26	74	24·00	23·15	21·22	15·29	25·30	27·96
6	13	87	34·74	33·72	33·12	29·66	35·61	38·06
7	0	100	36·03	30·56	40·25	46·74	62·51	43·72

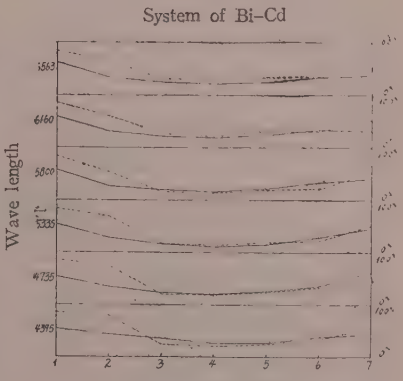
Fig. 8



Wave length

Reflective power after standing in *full* line.
Reflective power before standing in *dotted* line.

Fig. 7



Composition of alloys

Reflective power after standing in *full* line.
Reflective cower before standing in *dotted* line.

E. System of Bismuth and Tin.

Table IX

Relative Power in the Alloys of Bismuth and Tin

a. Immediately after Polishing

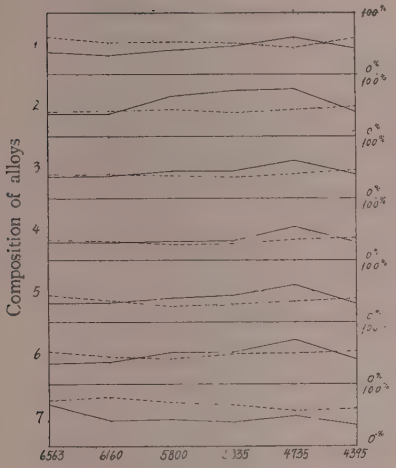
No.	Sample Composition		Reflective power in % for wave length						
	Sn in %	Bi in %	6563	6160	5800	5335	4735	4395	4105
1	0	100	60·75	52·31	53·48	51·25	44·68	59·91	54·72
2	13	87	39·35	41·60	44·16	38·64	43·63	49·02	44·79
3	27	73	38·77	38·46	37·53	34·18	40·89	46·78	42·32
4	42	58	32·09	31·27	25·30	27·24	33·18	37·21	31·68
5	62	38	43·27	35·07	26·88	29·00	34·70	38·67	32·96
6	81	19	52·92	44·79	41·32	48·32	50·67	58·30	54·27
7	100	0	73·14	78·10	70 91	67·52	57·10	61·81	59·34

b. After standing in a room at 26° C. with 3·4 % CO_2 and 76·19 moisture in terms of relative humidity

No.	Sample Composition		Reflective power in % for wave length					
	Sn in %	Bi in %	6563	6160	5800	5335	4735	4395
1	0	100	36·03	30·56	40.25	46·74	62·51	43·72
2	13	87	36·73	36·79	65·11	74·35	77·36	40·24
3	27	73	35·84	36·48	43·05	44·64	62·35	38·96
4	42	58	28·47	28·72	30·80	32·30	54·83	29·66
5	62	38	30·27	32·91	39·36	43·57	50·29	30·66
6	81	19	33·57	36·36	51·10	52·63	72·39	40·18
7	100	0	64·78	42·10	43·34	39·69	49·91	33·52

Fig. 10

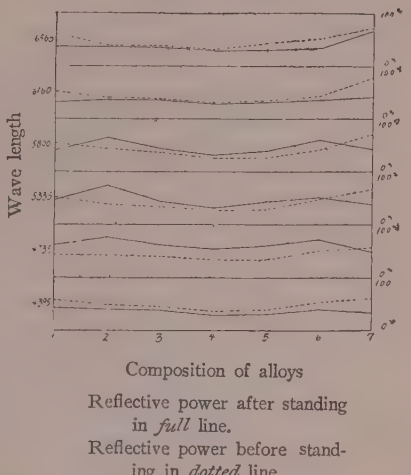
System of Bi–Sn



Reflective power after standing in *full* line.
Reflective power before standing in *dotted* line.

Fig. 9

System of Bi–Sn



Reflective power after standing in *full* line.
Reflective power before standing in *dotted* line.

From these results with the aid of the graphs, the following conclusions may be deduced :—

1. the degree of tarnishing is always specific with respect to a corresponding wave length, but
2. it shows some regularity in each system of the alloys;
3. with pure metals, the tendency of tarnishing is different from those of their alloys;
4. by comparing the values of the reflective powers of a sample, when polished and tarnished, for any wave length, the change of colour of a metallic surface may be determined.

The investigator wishes to express his thanks to Professor M. Chikashige for his valuable suggestions and kindly help throughout the course of this work.

Studies in Micro-Estimation of Metallic Elements. Part I. The Micro-Chemistry of Potassium Ferrocyanide.

By

Rokuro Nakaseko.

(Received December 13, 1927)

For the purpose of ascertaining the conditions under which the potassium ferrocyanide test for iron, copper, and zinc is most sensitive, and of obtaining an idea as to what extent this test can be adapted to the estimation of minute quantities of these metals, the following series of experiments were instituted.

A. The Potassium Ferrocyanide Reagent.

I. The Detection of Minimum Quantities of Iron with Potassium Ferrocyanide.

When 0·005 mg. of Fe is contained in 5 cc. of water acidulated with 2 drops of 6–N hydrochloric acid the blue color produced in 1–2 minutes by 1 cc. of 0·1–N ferrocyanide reagent is quite distinct when viewed sidewise. One part of Fe in 1,000,000 parts of water is thus easily detectable.

If this experiment is made in a neutral solution, there is no development of the blue color even after 20 minutes. The presence of a slight acidity—0·12–N in this case—is necessary for this delicate test of iron with the ferrocyanide reagent. This fact becomes very striking when compared with the seemingly contradictory fact presented later on that, in testing ferrocyanide in minute quantities with the ferric chloride

reagent, the presence of acidity in the solution hinders to a remarkable degree the development of the blue color.

Ferric chloride solution was tested in various dilutions, with or without acidulating with hydrochloric acid, with 1 cc. of 0·1–N potassium ferrocyanide reagent. The results are shown in the following table:

No.	$FeCl_3$ solution		1 part of Fe in parts of solution	Final acidity	Time of appearance of distinct blue color
	cc.	mg. Fe			
1	5	0·0050	1,000,000	0·1–N	1–2 minutes
2	5	0·0025	2,000,000	0·1–N	4 〃
3	5	0·0017	3,000,000	0·1–N	15 〃
4	5	0·0013	4,000,000	0·1–N	Not at all even after 30 minutes.
5	5	0·0008	6,000,000	0·1–N	Not at all even after 30 minutes.
6	5	0·0050	1,000,000	neutral	Not at all even after 30 miuutes.
7	5	0·0025	2,000,000	neutral	Not at all even after 30 minutes.
8	5	0·0017	3,000,000	neutral	Not at all even after 30 minutes.

According to this series of experiments, the minimum quantity of iron detectable with potassium ferrocyanide is 0·0017 mg. in 5 cc. of the test solution, i. e. 1 part of iron in 3,000,000 parts of the solution.

II. The Detection of Potassium Ferrocyanide with Ferric Chloride.

The standard tenth normal potassium ferrocyanide reagent was made by dissolving 10·559 g. of the crystallized salt in water and diluting to one liter. Starting with this stock solution, solutions of varying dilutions were made as follows:

Normality desired	Solution taken		Diluted to cc.
	normality	cc.	
N/1000	N/100	10	100
N/2000	N/1000	5	10
N/4000	N/100	12·5	500
N/5000	N/100	10·0	500
N/6000	N/100	8·3	500
N/8000	N/4000	5	10
N/10,000	N/5000	5	10
N/12,000	N/6000	5	10
N/15,000	N/5000	5	15

The ferric chloride solution was made in three strengths:

a. Containing 10 mg. Fe in 1 cc., (0·5 mg. in 1 drop).
b. Containing 1 mg. Fe in 1 cc., (0·05 mg. in 1 drop).
c. Containing 0·1 mg. Fe in 1 cc., (0·005 mg. in 1 drop).

The uranium nitrate solution was prepared by dissolving 1·5 g. of the salt in 10 cc. of water.

To show which of the above three dilutions of ferric chloride solution was most suitable for the detection of minute quantities of potassium ferrocyanide the following comparison was made with the N/5000 solution as the basis:

1. THE SPOT TEST. Spots of 3 drops of N/5000 ferrocyanide solution were treated on the test plate with one drop of one of the ferric chloride solutions. For the comparison's sake, the parallel test was made with a drop of the uranium nitrate solution and the blank test with drops of pure water. The results are shown in the following table:

$K_4Fe(CN)_6$ N/5000	Water	Fe added as $FeCl_3$	Uranium nitrate	Depth of color
3 drops		0.005 mg.		deepest blue
3 drops		0.05 mg.		blue
3 drops		0.5 mg.		deeper blue
3 drops			1 drop	yellow
	3 drops		1 drop	yellow

As seen from the table, for the purpose of spot testing of very dilute solutions of potassium ferrocyanide, 0·005 mg. of Fe is just as efficient as 0·05 mg. and 0·5 mg. The greater reactivity accompanying the greater concentration of Fe ion is counter-balanced by the deeper brown color which covers the blue color developed. It is also found that the uranium solution is of no use at all for the spot test of very dilute solutions here concerned.

The table below shows the results of the spot tests made with varying dilutions of the ferrocyanide solution. One drop of ferric chloride solution added contained always 0·05 mg. of Fe. Comparison is also made between the spots with 1 drop of 0·6–N HCl added and those without any acid. The remarkable hindering influence of an acidity upon the development of blue color is thus made striking to the eye.

It must be specifically noted here that, in making the spot tests as well as the "test tube tests", one and the same stock solution of $FeCl_3$ must

be drawn upon throughout the whole series of experiments that are compared with each other. One sample of ferric chloride solution may differ from another in its acidity and this slight difference may cause a wide deviation in the result. The experimenter's eye must also be standardized, so to speak, by a short practice upon known dilutions before the test is applied upon an unknown sample, for a person's color sensitivity may differ at different times.

$K_4Fe(CN)_6$		0.6–N HCl	Fe	Time of Color Appearance	
dilution	drops	drop	mg.	very faint blue	distinct blue
N/4000	2		0.05	10 seconds	30 seconds
N/5000	2		0.05	15 〃	50 〃
N/6000	2		0.05	20 〃	60 〃
N/8000	2		0.05	40 〃	90 〃
N/10000	2		0.05	3 minutes	
N/12000	2		0.05	7 minutes	
N/4000	2	1	0.05	5 minutes	
N/5000	2	1	0.05	5 minutes	
N/6000	2	1	0.05	No color even after 20 minutes.	
N/8000	2	1	0.05	No color even after 20 minutes.	

2. **The test tube test.** In the table below are given the results of parallel experiments with 3 cc. of N/5000 ferrocyanide solution tested with varying quantities of Fe as ferric chloride. The effect of addition of one drop of 6–N HCl is also contrasted with that in absence of the acid. These results are then compared with those obtained with uranium solution in place of ferric chloride.

It is clearly seen from the table that the presence of an acidity of about 0.1–N in HCl hinders to a remarkable degree the development of the characteristic blue color. Where, without HCl, a faint blue is immediately developed, there are required 30 minutes in the presence of 0.1–N final acidity.

Uranium nitrate test is very sharp with the test tube test for dilutions down to N/5000 of the ferrocyanide solution. But it is not any sharper than that with ferric chloride as to justify its sole use to the exclusion of the latter. Moreover, it is useless for greater dilutions than N/5000.

It is to be noted from the table below that the more concentrated ferric chloride solutions cause an earlier and more distinct blue color than

$K_4Fe(CN)_6$ N/5000	Water	Fe	Uranium nitrate	6–N HCl	Color appearance time
		mg.	drop	drop	
3 cc.		0·005			immediate faint blue.
3 cc.		0·05			immediate and very distinct blue.
3 cc.		0·5			immediate and decidedly distinct blue.
3 cc.		0·005		1	very faint blue in 30 minutes.
3 cc.		0·05		1	very faint blue in 20 minutes.
3 cc.		0·5		1	distinct blue in 10 minutes.
	3 cc.		1		no coloration.
3 cc.			1		immediate and very distinct yellow.

the weaker solution.

The table below summarises the results of parallel experiments with 5 cc. each of the various dilutions of the ferrocyanide solution. No hydrochloric acid was added. One drop of ferric chloride solution contained 0·05 mg. of Fe. In these experiments, the test tubes made of colorless glass, 17 by 8 mm. in size and of 25–27 cc. capacity, were found to be most suitable for color comparison. After a few experiments the test tubes are apt to be stained with incrustations of the Prussian blue which can be removed only by treatment with sodium hydroxide solution and a subsequent washing with hydrochloric acid.

$K_4Fe(CN)_6$		Fe added	Time of color appearance.		
dilution	cc.	mg.	very faint	faint	distinct
N/4000	5	0·05			Immediate and very distinct
N/5000	5	0·05			Immediate and distinct
N/6000	5	0·05	2 seconds		5 seconds
N/7000	5	0·05	5 seconds		10 〃
N/8000	5	0·05	7 〃		15 〃
N/9000	5	0·05	10 〃		30 〃
N/10000	5	0·05	20 〃		40 〃
N/12000	5	0·05	40 〃		1½ minutes
N/15000	5	0·05	1 minutes		2 〃
N/18000	5	0·05	2 〃		5 〃
N/20000	5	0·05	3 〃		10 〃
N/24000	5	0·05	10 〃	20 min.	

3. Influence of acidity upon the sensitivity of color reaction. In order to ascertain the degree of sensitivity of the ferrocyanide color reaction toward change of acidity, the experiments summarised in the tables below were instituted. For avoiding complexity of presentation only the dilution of N/4000 was chosen as the basis of this study. The volume of the solution was always 5 cc. and ferric chloride added was always equal to 0·05 mg. of Fe.

N/4000 $K_4Fe(CN)_6$	0·1–N HCl	Final acid normality	Time of appearing of faint blue	About comparable to neutral solution of normality
cc.	drops			
5	1	N/1000	Immediate and very distinct	N/4000
5	2	N/500	Immediate and very distinct	N/4000
3	3	N/333	Immediate and distinct	fainter than N/4000
5	5	N/200	Immediate and faint	N/5000
5	7	N/143	2 seconds	N/6000
5	8	N/125	2 seconds	N/6000

N/4000 $K_4Fe(CN)_6$	1–N HCl	Final acidity	Time of appearing of faint blue	Comparable to neutral solution of normality
cc.	drops			
5	1	N/100	2 seconds	N/6000
5	2	N/50	5 〃	N/7000
5	3	N/33	7 〃	N/8000
5	4	N/25	20 〃	N/10000
5	5	N/20	25 〃	N/11000
5	6	N/17	40 〃	N/12000
5	12	N/8	5 minutes	N/20000

4. Influence of salt concentration upon the color reaction.

It was found that presence of salts in different concentrations caused hindering effects in different degrees upon the development of blue color by the action of 0·05 mg. of Fe upon the N/4000 solution of potassium ferrocyanide. Such effects in the case of ammonium chloride and sodium chloride are summarized in the following tables:

a. *Ammonium Chloride.* The ammonium chloride solution was made in two concentrations—5–N and 0·5–N—which were added in different numbers of drops to 5 cc. of N/4000 potassium ferrocyanide.

0·05 mg. of Fe was then added and the time of color development was observed. The Cl ion normality was calculated in the final volume.

N/4000 $K_4Fe(CN)_6$ cc.	NH_4Cl solution		Cl ion normality –N	Time of color development	
	5–N drops	0·5–N drops		faint	distinct
5	0		·00	immediate	immediate
5	1		·05	15 seconds	30 seconds
5	2		·10	1½ minutes	4 minutes
5	3		·15	3 "	7 "
5	4		·20	4 "	8 "
5	5		·24	7 "	10 "
5	6		·30	8 "	15 "
5	10		·45	20 "	30 "
5	15		·68	20 "	30 "
5	20		·83	20 "	30 "
5		1	·005	immediate	immediate
5		2	·01	immediate	3 seconds
5		3	·015	2 seconds	4 "
5		4	·02	3 "	5 "
5		5	·024	5 "	10 "
5		7	·034	7 "	15 "
5		9	·041	8 "	20 "
5		10	·045	12 "	25 "

b. *Sodium Chloride.* The sodium chloride solution was also made in two dilutions—3·4–N and 0·34–N—which were added in various numbers of drops to 5 cc. of N/4000 potassium ferrocyanide. One drop of ferric chloride containing 0·05 mg. of Fe was added and the time of color development observed. The normality of Cl ion was calculated in the final volume.

N/4000 $K_4Fe(CN)_6$ cc.	NaCl solution		Cl ion normality –N	Time of color development	
	0·34–N drops	3·4–N drops		faint	distinct
5	1		·003	immediate	immediate
5	2		·007	immediate	3 seconds
5	3		·01	3 seconds	5 "
5	4		·013	3 "	5 "
5	5		·017	3 "	5 "
5	6		·02	4 "	7 "
5	7		·023	5 "	10 "
5	8		·027	6 "	10 "
5	9		·03	7 "	12 "

5	1	·034	10 〃	15 〃
5	2	·068	40 〃	90 〃
5	3	·10	1½ minutes	2½ minutes
5	4	·13	2 〃	3 〃
5	5	·17	3 〃	5 〃
5	6	·2	7 〃	10 〃
5	7	·23	8 〃	12 〃
5	8	·27	16 〃	20 〃

By examining the above two tables, the fact becomes very obvious that there runs a close parallelism between the effects of ammonium chloride and sodium chloride upon development of blue color by potassium ferrocyanide. A very natural conclusion is that the hindering influence of these salts is chiefly due to the concentration of the chlorine ion.

5. Influence of 0·6-N hydrochloric acid upon the time of color development of potassium ferrocyanide under the action of ferric chloride. In the following series of experiments a definite volume of potassium ferrocyanide solution of varying normality was mixed with 2 cc. of 6–N HCl and the mixture diluted to 20 cc. The normality of HCl was now exactly 0·6–N, and the normality of $K_4Fe(CN)_6$ was calculated out. 5 cc. of such a mixture were treated with 0·05 mg. of Fe and the time of initial color appearing was noted.

Final normality		Time of color development	
$K_4Fe(CN)_6$	HCl	faint	distinct
N/500	0·6–N	immediate	immediate
N/600	0·6	immediate	2 seconds
N/700	0·6	3 sec.	7 〃
N/800	0·6	5 〃	7 〃
N/900	0·6	7 〃	10 〃
N/1000	0·6	12 〃	15 〃
N/1100	0·6	12 〃	17 〃
N/1200	0·6	13 〃	17 〃
N/1500	0·6	25 〃	40 〃
N/1800	0·6	50 〃	70 〃
N/2000	0·6	1½ min.	2 minutes
N/3000	0·6	10 〃	15 〃
N/4000	0·6	indefinite	indefinite.

6. **The joint influence of 0·6–N hydrochloric acid and 0·5–N ammonium chloride upon the time of color development of potassium ferrocyanide.** In the experiments tabulated below, $K_4Fe(CN)_6$ solutions of varying normalities were mixed with 2 cc. of 6–N HCl and 2 cc. of 5–N NH_4Cl and then diluted to 20 cc. 5 cc. of such a solution were then treated with 0·05 mg. of Fe and the time of the initial appearance of the blue color noted.*

Final normality			Time of initial color development	
$K_4Fe(CN)_6$	HCl	NH_4Cl	faint	distinct
N/300	0·6	0·5	immediate	3 seconds
N/400	0·6	0·5	4 seconds	6 "
N/500	0·6	0·5	5 "	7 "
N/600	0·6	0·5	9 "	12 "
N/700	0·6	0·5	14 "	18 "
N/800	0·6	0·5	18 "	23 "
N/900	0·6	0·5	25 "	32 "
N/1000	0·6	0·5	35 "	45 "
N/1100	0·6	0·5	55 "	70 "
N/1200	0·6	0·5	65 "	80 "
N/1500	0·6	0·5	2 minutes	3 minutes
N/1800	0·6	0·5	3 "	4½ "
N/2000	0·6	0·5	5 "	6½ "
N/3000	0·6	0·5	15 "	24 "
N/4000	0·6	0·5	25 "	35 "

III. The Spontaneous Change of Potassium Ferrocyanide Reagent.

The ferrocyanide reagent undergoes a rather rapid spontaneous change in acidulated state, developing a blue color and depositing a precipitate of Prussian blue. Several series of experiments were performed for the purpose of ascertaining the conditions of this change.

1. Three parallel experiments were carried out in the diffused

* A similar study was also made upon the influences of 0·6–N NH_4Cl and of 1·1–N NH_4Cl on the time of the initial color appearance of potassium ferrocyanide solution under the action of ferric chloride solution. Space does not permit to enter into their discussion here.

day-light at 60° with solutions mixed in such a manner as to result in the final normality given in the table below. After the lapse of one hour there was no change of color observed. After one and a half hours the solutions assumed a very distinct blue color to a nearly equal depth. On centrifugating, the second tube was found to have developed a very minute trace of blue precipitate. They were centrifugated after 3 hours and each of the solutions was found to have deposited some minute quantity of blue precipitate. After 4 hours, there accumulated some blue sediment at the bottom and there floated some flocky particles in the liquid. Upon centrifugation after 30 hours, the color of the liquids still remained intensely blue.

Final normality		Total volume cc.	Observed after		Centrifugated after		
$K_4Fe(CN)_6$	HCl		1 hr.	1½ hrs.	1½ hrs.	4 hrs.	30 hrs.
0.19-N	0.3	10.5	no color	blue	no ppt.	blue ppt.	intensely blue ppt.
0.095-N	0.6	10.5	no color	blue	minute ppt.	blue ppt.	intensely blue ppt.
0.095-N	0.3	10.5	no color	blue	no ppt.	blue ppt.	intensely blue ppt.

2. In order to ascertain the nature of influence exerted by light upon the spontaneous change of the acidulated ferrocyanide solution, the following experiments were carried out at room temperature.

20 cc. of water were acidulated with 10 drops of 6–N HCl, treated with 8 drops of 1–N potassium ferrocyanide solution, and divided into four aliquots of 5.2 cc. each. Two of them were exposed to the direct sun-light inside of the window glass. The other two were well wrapped up with black paper and set aside in a corner of a dark closet. The result is summarized in the following table :

Final normality		Direct sun-light	½ hr.	1 hr.	2 hrs.	50 hrs.
$K_4Fe(CN)_6$	HCl					
0.024-N	0.15-N	exposed	no change	blue	intnesely blue ppt.	abundant blue ppt.
0.024-N	0.15-N	left in the dark	no change	no change	no change	no change

3. A dilute neutral solution of potassium ferrocyanide undergoes no appreciable change by keeping it for days and months in the diffused day light unless acted upon by acid fumes when it may deposit blue

incrustation at the mouth of the bottle containing it.

Very dilute neutral solutions of potassium ferrocyanide undergo, however, another kind of spontaneous decomposition by a long keeping in the diffused day light. By this change there is no production of Prussian blue, but the salt is split up hydrolytically and deposits a brownish yellow precipitate of ferrous cyanide, probably according to the equation :

$$K_4Fe(CN)_6 + 4H_2O = Fe(CN)_2 + 4KOH + 4HCN,$$
$$HCN + 2H_2O = HCOONH_4.$$

a. N/4000 potassium ferrocyanide solution containing 2·6 mg. of the salt in 100 cc. was found to have deposited, on being allowed to stand in the reagent shelf for 5 months, a brownish yellow precipitate leaving the supernatant liquid clear and transparent but very faintly yellowish. 5 cc. of the solution tested with 1 drop of ferric chloride solution developed a very faint blue in 20 minutes showing that it was now in concentration less than N/24000. The brownish yellow precipitate was separated and washed by centrifugation. When dissolved in dilute HCl and tested with 0·1–N potassium ferrocyanide solution, it gave an intense blue color characteristic of iron.

b. N/5000 potassium ferrocyanide solution containing 2 mg. of the salt in 100 cc. has not deposited any precipitate after being allowed to stand for 5 months. But it has become distinctly opalescent with yellowish tinge.

c. N/6000 potassium ferrocyanide solution containing 1·66 mg. of the salt in 100 cc. has deposited after 5 months' standing a yellowish brown precipitate of $Fe(CN)_2$. 5 cc. of the clear colorless solution tested with 1 drop of ferric chloride solution developed no blue color even in 2 hours, showing that practically all the salt had been decomposed hydrolytically by this time.

B. The Micro-Estimation of Zinc with Potassium Ferrocyanide.

a. Zinc sulfate solution containing 0·25 mg. of Zn in 1 cc. and 0·0125 mg. of zinc in one drop was used for the following experiments.

One drop of the zinc solution was added to a mixture of 1 cc. of water and 2 drops of 6–N HCl (making the resulting acidity 0·6–N). One drop of 1–N potassium ferrocyanide was then added. The white turbidity which was formed immediately was compared with the similar

turbidity formed with two drops and three drops of the zinc solution mixed with 1 cc. each of water acidified with 2 drops of 6–N HCl and one drop of 1–N potassium ferrocyanide. It was found that the turbidity varied in thickness regularly in proportion to the concentration of zinc in the mixture.

After allowing the tubes to stand for one hour, they were centrifugated and the volumes of the precipitate were compared with each other. It was found here again that the apparent volumes of the white zinc ferrocyanide precipitate in the three tubes differed regularly according to the quantities of zinc contained in the original mixtures.

Minute quantities of zinc down to 0·01 mg. can be thus easily detected and compared with each other both by the thickness of turbidity and by the size of the centrifugated precipitate. For this latter purpose the centrifuge tubes whose bottoms are drawn to a rather narrow bore are to he recommended, as were proposed by Hamburger[1], Breukeleveen[2], and the present author[3].

b. In order to ascertain the difference of action, in a neutral and acid medium, of a minute quantity of zinc upon potassium ferrocyanide the following experiments were instituted:

To each of the first set of two tubes, there were added 1 cc. of 0·1–N $K_4Fe(CN)_6$ solution and 1 cc. of neutral zinc acetate solution containing 0·25 mg. of Zn. In these neutral mixtures there appeared immediately a white turbidity which began to settle down as a pale white precipitate only upon the lapse of a few days. When the tubes were allowed to stand in the direct sun light for several hours there was noted no change of color to take place in them. After being allowed to stand in the diffused day light for two months the precipitate remained just as white as at the beginning. The supernatant liquid which was yellow gave a strong reaction with ferric chloride solution showing that there was a great excess of potassium ferrocyanide remaining perfectly intact.

To each of the second set of two tubes, there were added 1 cc. of 0 1–N $K_4Fe(CN)_6$ acidulated with 1 drop of 6–N HCl and 1 cc. of zinc acetate solution containing 0·25 mg. of Zn. The turbidity that appeared immediately was denser and whiter than in the neutral medium of the first set. By keeping the tubes in the dark closet for 28 hours the white precipitate collected in the bottom leaving the supernatant liquid clear and yellow. When the tubes were now exposed to the direct sun light

1 Recueil d. Trav. Chim., **35**, 225–253 (1916).
2 Ibid., **36**, 285 (1917).
3 These Memoires, **3**, 101–109 (1918).

for two hours, the whole content turned deep blue leaving the precipitate perfectly white. After allowing them to stand on the laboratory desk for two months, they were centrifugated. The clear solutions thus separated were now perfectly colorless and they gave no blue coloration either with ferric or ferrous salt solution, showing that all the ferrocyanide ion in the acid medium was completely decomposed and precipitated by the action of light in the course of the two months.

C. The Micro-Volumetry of Zinc with Potassium Ferrocyanide.

As it was shown by Waring[1] the reaction between zinc solution and ferrocyanide solution takes place in two steps. In the cold the reaction first stops at the stage,

$$2Zn(CH_3CO_2)_2 + K_4Fe(CN)_6 = Zn_2Fe(CN)_6 + 4CH_3COOH.$$

This first reaction product, normal zinc ferrocyanide, is a flocky precipitate easily settling on the bottom. When it is left standing in contact with excess of potassium ferrocyanide in the cold, it is slowly changed to a very finely divided milky state, when it readily passes through the filter paper and now it is impossible to separate it by means of filtration. This change of the flocky precipitate into a milky, filter-passing state takes place instantly when the reaction mixture is at near the boiling point. This second stage of reaction is represented by the equation:

$$3Zn_2Fe(CN)_6 + K_4Fe(CN)_6 = 2Zn_3K_2[Fe(CN)_6]_2.$$

The quantity of potassium ferrocyanide consumed in the second stage is theoretically just one-third that of the first stage. When the reaction is caused to take place in the boiling solutions, the sudden transition from the first to the second stage is very easily observed. It is in this second phase of change that the reaction mixture can be subjected to the turbidimetric comparison with similar mixtures from known quantities of zinc.

A series of experiments were instituted to see whether the well-known method of volumetry of zinc according to the above reaction could be so modified as to adapt it to the determination of very minute quantities of zinc.

The stock solution of zinc acetate was prepared by dissolving 9·6067 g. of pure ignited zinc oxide in 100 cc. of 30 per cent. acetic

1 J. A. C. S., **26**, 4–29 (1904).

acid and diluting to 1 liter. One cc. of this solution contained 7·718 mg. of Zn. 32 cc. of it containing 250 mg. of Zn were now diluted to 1 liter to obtain the standard solution containing 0·25 mg. of Zn in 1 cc. and 0·0125 mg. of Zn in 1 drop.

I. The Micro-Volumetry of Zinc with Ferric Chloride as the External Indicator.

a. A series of seven graduated centrifuge tubes were arranged in a row. Varying numbers of cc. of the standard zinc solution were measured into them. After adding to each 1 cc. of 5–N NH_4Cl solution, the tubes were filled to 7 cc. mark with distilled water; two cc, of N/50 $K_4Fe(CN)_6$ solution were then added and the mixtures inserted to the water bath at 80° and left in the dark closet until the temperature fell to 40° in about 30 minutes. The precipitate was now flocky and easily coagulated. One cc. of 6–N HCl was finally added when the whole passed into a dense milky condition. The tubes were again inserted into the water bath at 80° and left in the dark closet for about 30 minutes more until the temperature fell to 40°. They were then centrifugated at last.

5 cc. of the clear and colorless solution were pipetted out of each of the seven tubes and subjected to the "test tube test" with 0·05 mg. of Fe. The results were compared with the data given in the table on p. 9 and the normalities of $K_4Fe(CN)_6$ remaining unacted upon were thus found out. The details of these experiments are made more readily intelligible in the following table:

No.	Zinc solution	Zn taken	Final normality		N/50 $K_4Fe(CN)_6$	Latent time of color development.		Final $K_4Fe(CN)_6$ normality
	cc.	mg.	NH_4Cl	HCl	cc.	faint	distinct	
1	2·0	0·50	0·5–N	0·6–N	2	8 sec.	10 sec.	N/580
2	2·2	0·55	0·5	0·6	2	10 〃	15 〃	N/620
3	2·6	0·65	0·5	0·6	2	15 〃	20 〃	N/720
4	2·8	0·70	0·5	0·6	2	30 〃	40 〃	N/950
5	3·4	0·85	0·5	0·6	2	5 min.	6½ min.	N/2000
6	3·6	0·90	0·5	0·6	2			N/5000
7	3·9	0·98	0·5	0·6	2			

In the tube No. 6, the normality in $K_4Fe(CN)_6$ of the final solution was

too small to respond to the "test tube test", and, therefore, it was infered from the result of evaporating the acidified solution to dryness in strong sun light. The normality was judged by the depth of the blue color thus developed. The No. 7 utterly failed to give even this most delicate test for $K_4Fe(CN)_6$.

From the final normalities thus found the amounts of zinc originally taken for estimation were calculated according to the equation:

$$(a-50bv)\times d = \text{total wt. of Zn.}$$

where a is the number of cc. of the N/50 $K_4Fe(CN)_6$ that was added;
b is the normality of $K_4Fe(CN)_6$ found in the final solution;
v is the total volume of the reacting mixture (10 in this case);
d is mg. of Zn equivalent to 1 cc. of N/50 $K_4Fe(CN)_6$, which was found to be 0·47 mg. in these experiments.

As a was equal to 2 in these experiments the above general formula could be written in the more practical shape as follows:

$$(2-500\ b)\times 0{\cdot}47 = \text{total weight of Zn found.}$$

The results of calculations made from the above given data according to the practical formula here deduced are summarized in the following table:

No.	b found	500 b found	Zn found mg.	Zn taken mg.	Error mg.	The maximum error
1	1/580	0·862	0·536	0·50	0·036	
2	1/620	0·807	0·564	0·55	0·014	
3	1/720	0·700	0·611	0·65	0·039	0·039 mg.
4	1/950	0·530	0·691	0·70	0·009	
5	1/2000	0·250	0·823	0·85	0·027	
6	1/5000	0·100	0·893	0·90	0·007	

b. A second series of determinations were carried out in a manner very similar to the first, taking much smaller quantities of zinc ranging between 0·5 mg. and 0·025 mg. The amount of N/50 $K_4Fe(CN)_6$ taken was 1 cc. The mixtures were inserted into the water bath at 80° and allowed to gradually cool down while standing over-night in the dark closet.

From the final normalities of $K_4Fe(CN)_5$ remaining unacted upon, the amounts of zinc that had existed at the commencement of the

No.	Zinc solution	Zn taken	Final normality		N/50 $K_4Fe(CN)_6$	Latent time of color development		Final $K_4Fe(CN)_6$ normality
	cc.	mg.	NH_4Cl	HCl	cc.	faint	distinct	
1	2·0	0·5	0·5–N	0·6–N	1			N/5000
2	1·6	0·4	0·5	0·6	1	25 min.	30 min.	N/4000
3	1·2	0·3	0·5	0·6	1	1½ 〃	2 〃	N/1300
4	0·8	0·2	0·5	0·6	1	30 sec.	25 sec.	N/900
5	0·4	0·1	0·5	0·6	1	15 〃	20 〃	N/700
6	0·2	0·05	0·5	0·6	1	10 〃	15 〃	N/600
7	0·1	0·025	0·5	0·6	1	9 〃	12 〃	N/600

experiments were calculated according to the same process as was explained on p. 15, applying the formula

$$(a - 500\,b) \times 0{\cdot}47 = \text{total wt. of Zn.}$$

In this case the value of "a" [the number of cc. of the N/50 $K_4Fe(CN)_6$] was 1. The results are summarized in the following table :

No.	b found	500 b found	Zn found mg.	Zn taken mg.	Error mg.	The maximum error
1	1/5000	1/100	0·47	0·50	0·03	With quantities of zinc ranging between 0·5 mg. and 0·05 mg. the maximum error is 0·03 mg.
2	1/4000	1/8	0·41	0·40	0·01	
3	1/1300	5/13	0·29	0·30	0·01	
4	1/900	5/9	0·21	0·20	0·01	
5	1/700	5/7	0·13	0·10	0·03	
6	1/600	5/6	0·08	0·05	0·03	
7	1/600	5/6	0·08	0·025	0·06	

c. Incidentally, it may be pointed out here that in the second series of experiments here described on p. 15, the seven tubes differed from each other in a very regular gradations in the thickness of the turbidity of the reaction mixtures. Quantities of zinc ranging between 0·5 mg. and 0·05 mg. can, therefore, be easily differentiated and estimated by means of this method by comparing their turbidities with those produced by the known quantities of the metal. With quantities above 0·5 mg. of Zn, the turbidities produced in the volume of 10 cc. of the mixtures are not easily differentiated one from the other.

II. A Procedure of Micro-Volumetry of Zinc with Potassium Ferrocyanide and Ferric Chloride.

The procedure of the methods described above can be formulated as follows:

Evaporate the solution to be tested for zinc and freed from iron and manganese to dryness and ignite to expel any excess of acids, ammonia, or ammonium chloride. Take up the residue in 2 cc. of water and add 1 cc. of 6–N HCl and 1 cc. of saturated (5–N) ammonium chloride measured in a pipette. Add now one, two, or more cc. of N/50 potassium ferrocyanide solution carefully measured from a burette. The addition of potassium ferrocyanide should be done drop by drop with constant stirring, and it should be stopped when the precipitate formed has completely passed from the flocky or granular state to the milky and colloidal condition. As the precipitate begins to pass from the first to the second state when three-fourths of the necessary quantity of potassium ferrocyanide have been consumed, this will afford a proper land-mark for judging approximately the necessary amount to be added. The whole mixture is now filled up to exactly 10 cc., and inserted into the water bath at 60–70° and allowed to stand in the dark closet for 30 minutes.

The mixture is now centrifugated and the clear colorless supernatant liquid poured into a test tube. A few drops of the liquid are taken to the spot test plate and tested with ferric chloride solution, each drop of which contains 0·05 mg. of Fe. The result of this spot test should be judged by refering to the table appended to the end of this chapter on p. 18.

Guided by the result of the spot test, the "test tube test" is performed upon a 5 cc. portion of the liquid using the table on p. 9 as the standard of reference. From the final normality of potassium ferrocyanide, the amount of zinc in the sample analyzed is calculated by using the formula:

$$(a - 500\,b) \times 0{\cdot}47 = \text{Wt. of zinc},$$

where "a" represents the number of cc. of the potassium ferrocyanide solution added, and "b" the final normality of potassium ferrocyanide remaining unacted upon. The figure "0·47" used in this formula represents the weight of zinc equivalent to 1 cc. of the N/50 potassium ferrocyanide solution.

THE SPOT TEST. For determining approximately the normality of the potassium ferrocyanide remaining unacted upon in the above

reaction, 2 drops of the clear and colorless centrifugated liquid are tested with 1 drop of ferric chloride and the normality is read from the following table :

The spot test table for $K_4Fe(CN)_6$ in the medium of 0·6–N HCl and 0·5–N NH_4Cl

No.	$K_4Fe(CN)_6$		$FeCl_3$ (0.05 mg. Fe)	Time of initial color development	
	normality	drops	drop	faint	distinct
1	1/250	2	1	immediate	immediate
2	1/500	2	1	1 sec.	2 eec.
3	1/750	2	1	2 〃	4 〃
4	1/1000	2	1	7 〃	12 〃
5	1/1250	2	1	30 〃	50 〃
6	1/1500	2	1	40 〃	100 〃
7	1/1750	2	1	2 min.	3 min.
8	1/2000	2	1	3 〃	4 〃

In conclusion the author desires to acknowledge his indebtedeness to Professor Motooki Matsui for his encouragement and advises throughout this investigation.

Studies in Micro-Estimation of Metallic Elements. Part II. The Micro-Detection of Iron with Dimethylglyoxime.

By

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The possibility of use of dimethylglyoxime for detection of a minute quantity of cobalt was pointed out by Prof. M. Matsui in 1918. He has also called attention to the production of a red color by the action of dimethylglyoxime upon a solution of ferrous salt when the mixture was treated with hydrogen sulfide and neutralized with ammonia. At his suggestion the following experiments were performed to ascertain the conditions of this reaction in more detail.*

I. The standard ferrous ammonium sulfate solution containing 0·1 mg. of Fe in 1 cc. was used as the stock solution for preparing various dilutions of the test solutions of iron. Dimethylglyoxime used was dissolved in alcohol to one per cent. strength. The hydrogen sulfide solution was always used in the freshly saturated state. The solutions were mixed in the order, from left to right, given in the table below, and the nature of the color developed was carefully noted 10 minutes after mixing the reagents.

With solutions containing 0·05–0·1 mg. of Fe in the final volume of 2·5 cc. there appeared, immediately on addition of saturated hydrogen sulfide solution, a more or less distinct opalescence due to the liberation of some free sulfur, which, however, caused no harm to the observation of the result.

* M. Matsui: J. Tokyo Chem. Soc., **39**, 463 (1918).

The solutions containing 0·4 and 0·2 mg. of Fe showed, when diluted to 50 cc., a presence of abundant minute black particles floating about but having no tendency to settle down. The color of the solution itself was dark wine red. On being allowed to stand several hours, the black particles have partly dissolved away and partly settled on the bottom.

The solution containing 0·1 mg. of Fe showed, when diluted to 50 cc. no black particles in it and the liquid was dark wine red. The solution containing 0·05 mg. of Fe was, when diluted to 50 cc., pure beautiful orange and became opalescent suddenly after 30 minutes.

The solutions containing in the final volume of 2·2 cc. 0·01 and 0·005 mg. of Fe were beautiful wine red. When diluted to 10 cc., the color changed to a very thin but pure orange. The solutions with 0·001 and 0·0005 mg. of Fe respectively in the final volume of 2·2 cc. were very faint orange which became only just barely perceptible by diluting to 10 cc.

No.	Fe taken mg.	H_2S cc.	Dimethyl-glyoxime drops	6-N ammonia drops	Final volume cc.	Color of the mixture after 10 minutes.
1	0·4	1	10	5	5·5	Intensely dark red, almost black.
2	0·2	1	10	4	3·5	Intensely dark red, almost black.
3	0·1	1	10	4	2·5	Intensely dark red.
4	0·05	1	10	3	2·3	Intensely dark red.
5	0·01	1	10	2	2·2	Brownish red.
6	0·005	1	10	2	2·2	Brownish red.
7	0·001	1	10	2	2·2	Slight pink orange.
8	0·0005	1	10	2	2·2	Very faint pink orange.
9	0·0001	1	10	2	2·2	Extremely faint orange.
10	0·00005	1	10	2	2·2	Almost imperceptibly faint orange.

The solutions containing in the final volume of 2·2 cc. 0·0001 and 0·00005 mg. of Fe respectively were extremely faint orange and well-nigh imperceptible unless a very close comparison was made with pure water. Thus, 5/100 000 mg. of Fe in 1 cc. of the original and in 2 cc. of the final volume is the minimum quantity detectable by means of the dimethylglyoxime reaction.

Quantities of Fe ranging between 0·1 and 0·01 mg. are best estimated

in the volume of 50 cc. by the colorimetric comparison of the dimethylglyoxime reaction. For quantities ranging between 0·001 and 0·01 mg. of Fe, a volume of 10 cc. is more suitable for the colorimetric purpose.

II. In the second series of experiments, the order of mixing the reagents was changed in such a manner as to make the saturated H_2S solution come at last. It was found that a mixture of iron solution and dimethylglyoxime reagent developed a beautiful reddish yellow on making it alkaline with ammonia. When H_2S was added to this solution, the color changed to dark green, separating at the same time minute black particles floating about without any tendency to settle down. When the quantity of H_2S added was small, the solution became opalescent in a few minutes; with a larger quantity of H_2S, opalescence did not appear within two hours.

No.	Fe taken	Dimethyl-glyoxime	6–N Ammonia	H_2S	Color developed	Opalescence appeared
	mg.	drops	drops	drops		
1	0·1	10	2	5	Reddish yellow by ammonia, changing to dark green by H_2S.	5 min.
2	0·1	10	2	10	The same as above	15 min.
3	0·1	10	2	15	The same as above	2 hrs.
4	0·1	10	2	20	The same as above	12 hrs.

III. For the purpose of ascertaining any difference, if there be, between ferrous and ferric salts in their dimethylglyoxime reaction, the following experiments were repeated several times always with the concordant results.

1. One cc. of ferrous ammonium sulfate solution containing 0·1 mg. of Fe was boiled with 1 cc. 1–N $NaHSO_3$ solution with addition of 1 drop of 6–N HCl. No change of color was observed by adding to this 10 small drops of dimethylglyoxime solution. There were now added 2–3 drops of ammonia, when a beautiful red color appeared, which changed, on addition of an excess of saturated H_2S, into a very dark brownish red. On dilution to 50–60 cc. the color changed to brownish orange.

2. One cc. of the solution containing 0·1 mg. of Fe was boiled with 2 drops of bromine water with addition of 1 drop of 6–N HCl. No change of color was noticed by adding to this 10 drops of dimethylglyoxime solution. By adding now 2–3 drops of 6–N ammonia,

there appeared a beautiful yellow color which changed, on addition of an excess of saturated H_2S, into a very dark green. By diluting to 50–60 cc., the color remained dark green almost without any tint of yellow or red. There were also noticed abundant black particles floating in the dark green solution. These particles were very light and did not show any tendency to settle down in the course of several hours. By allowing to stand over night, these particles were found to have partly dissolved away and partly settled on the bottom.

IV. A comparison of dimethylglyoxime and ammonium sulfocyanate as the reagents for micro-detection of iron was instituted. For testing with the former reagent the standard ferrous ammonium sulfate solution was diluted to such a strength as 1 cc. of it contained 0·001 mg. of Fe. For testing with the latter reagent, 2 cc. (0·002 mg. Fe) of the ferrous ammonium sulfate solution were boiled with 2 drops of bromine water and 2 drops of 6–N HCl, evaporated to near dryness, and made up to 2 cc. Four different quantities of each solution were taken for the testing purpose.

No.	Ferrous iron		H_2S	Dimethyl-glyoxime	6–N ammonia	Color	Color–maximum reached in
	solution	Fe					
	drops	mg.	cc.	cc.	drops		
1	20	0·001	1	1	2	Faint orange	2 hrs.
2	10	0·0005	1	1	2	Very faint orange	2 hrs.
3	2	0·0001	1	1	2	Extremely faint orange	2 hrs.
4	1	0·00005	1	1	2	Still perceptible orange	2 hrs.

No.	Ferric iron		Ammonium sulfocyanate	Color	Color–maximum reached in
	solution	Fe			
	drops	mg.	cc.		
1	20	0·001	1	Faint red	a few minutes.
2	10	0·0005	1	Very faint red	a few minutes.
3	2	0·0001	1	Extremely faint red	a few minutes.
4	1	0·00005	1	No color	

The detectability of iron, or the degree of color distinctness, with the both reagents was about the same when the quantities ranged between 0·001 and 0·0001 mg. of Fe. With 0·00005 mg. of Fe, the faint pink orange of dimethylglyoxime was barely but undubitably perceptible, while there was no color noticeable with NH_4SCN reagent.

SUMMARY

1. The color tone and the color depth produced by the action of dimethylglyoxime upon iron solutions change with the change of the order of mixing the reagents. But they remain constant so long as the concentration of the reagents and the order of mixing them remain the same.

2. If the dimethylglyoxime test of iron is made with a sufficient excess of H_2S, the color developed is very intense and it keeps well for twenty hours or more. The color depth is also proportional to the concentration of iron.

3. The presence of an excess of H_2S is also necessary to prevent the opalescence of the reaction mixture. The iron–dimethylglyoxime–hydrogen sulfide compound is rather unstable and, in small concentrations of H_2S, it fades in color and liberates sulfur as opalescence. When it has once undergone this change, the original color can no more be restored by again saturating the solution with H_2S.

4. For the purpose of colorimetric estimation of minute quantities of iron with dimethylglyoxime, the test solution should be first treated with saturated H_2S solution so as to reduce any ferric salt present to ferrous salt. The mixture should then be treated with dimethylglyoxime and finally with ammonia.

5. The applicability and utility of dimethylglyoxime and ammonium sulfocyanate for micro-colorimetry of iron are about the same in the both cases, although one may be used in preference to the other according to circumstances.

In conclusion the author wishes to express his deep gratitude toward Professor Motooki Matsui for his kind guidance and encouragement throughout these experimental studies.

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